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NUMBER THREE

RUBBER CHEMISTRY AND TECHNOLOGY

PUBLISHED QUARTERLY BY THE
DIVISION OF RUBBER CHEMISTRY
OF THE AMERICAN CHEMICAL SOCIETY



KOSMOS 60 RF
KOSMOS 60 RF



KOSMOS 60 RF
KOSMOS 60 RF

Kosmos 60 is today the most talked about furnace black for reinforcing natural and synthetic rubber. It originates from oil and is perfected by United's exclusive process. Its superb processing and balance of strength make for the best in rubber products.

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Back when most auto tires gave only 3,000 miles of service, Witco became a supplier of carbon black to the rubber industry. That was 1920. The subsequent development of reinforcing blacks for improved wearing qualities played a big role in the steady development of the rubber industry. Today, after contributing to the growth of carbon black usage for 35 years, WITCO-CONTINENTAL operates five up-to-date carbon black plants manufacturing a complete line of furnace and channel blacks.

Through the years, service has been an important part of our business at Witco-Continental. Customers have come to rely on our technical service laboratories for assistance with their problems. And they have found that it's easy to arrange prompt deliveries through our local sales offices in every major industrial area—nine in the U.S. and two in England.

Industry's call for more and more of our products has promoted a long-term growth pattern at Witco-Continental, one which is still in progress. By diversifying products and integrating service to meet the needs of the rubber and chemical manufacturers, Witco has shared in the fabulous growth of these industries.

It is significant that our 35th anniversary marks the most important years of progress in the industries we serve—as well as 35 years of growth for Witco.

For more information on WITCO-CONTINENTAL Carbon Blacks, send for literature or call our nearest sales office.

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35 Years of Growth

Entered as second-class matter March 19, 1943, at the Post Office at Lancaster, Pa., under the Act of August 24, 1912. Acceptance for mailing at special rate of postage provided for in paragraph (d-2), Section 3440, P. L. and R. of 1948, authorized September 25, 1940.

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By working with many grades of carbon blacks at various loadings and different acceleration rates . . . by determining moisture absorption and its effects . . . by collecting data on aging and tensile strength at high and low temperatures . . . by constantly experimenting, testing and checking results, Philblack scientists have amassed a wealth of information that is extremely valuable to manufacturers of rubber products.

Philblack customers can benefit from Phillips many years of research and practical experience in the carbon black field. If you would like to achieve certain characteristics in your finished product . . . reduce operational difficulties . . . or set up quality controls, consult your Philblack representative.



The electron microscope (50,000 X) shows that Philblack O is a fine particle black with moderate chain structure.

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KNOW WHAT THEY'LL DO FOR YOU!



Philblack A FEF Fast Extrusion Furnace Black

Ideal for smooth tubing, accurate molding, satiny finish. Mixes easily. High, hot tensile. Disperses heat. Non-staining.



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For long, durable life. Good electrical conductivity. Excellent flex. Fine dispersion.



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Toughest black on the market. Extreme abrasion resistance. Withstands aging, cracking, cutting and chipping.



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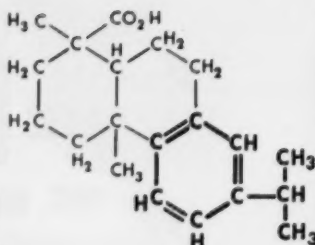
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plasticizer for
**GR-S, NEOPRENE,
NATURAL RUBBER
and RECLAIM**



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"Galex" is widely used as a tackifier-plasticizer in hose, belting, mechanical goods and various friction stocks. It imparts strong surface tack which develops into excellent adhesion after cure. "Galex" also functions as a highly stable and compatible tackifier in rubber-base adhesives and cements.

Write for technical information and samples.

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In Canada: Naugatuck Chemicals Division, Dominion Rubber Company, Elmira, Ontario

IMPORTANT NAMES to all users of synthetic rubbers are these designations for the various types of PLIOFLEX—Goodyear Synthetic Rubber:



PLIOFLEX 1000—
hot, nonpigmented,
staining type

PLIOFLEX 1006—
hot, nonpigmented,
nonstaining type

PLIOFLEX 1502—
cold, nonpigmented,
nonstaining type

PLIOFLEX 1703—
cold, oil masterbatch
(25 parts oil),
nonstaining type

PLIOFLEX 1710—
cold, oil masterbatch
(37½ parts oil),
staining type

THIS HOME OF QUALITY

is now the home of

Plioflex

UNDER Government ownership, this former GR-S plant in Houston, Texas, became well-known for its unusually high quality rubber. Now its standards are going even higher. Now, it is the home of PLIOFLEX.

PLIOFLEX is the designation for a family of styrene rubbers. Basically the same rubbers in production when the plant changed hands, they include "hot," "cold" and oil extended types, with emphasis on the light-colored nonstaining polymers.

But higher quality and uniformity are only two of the objectives in making PLIOFLEX. PLIOFLEX also brings you complete technical service, improved packaging and rapid, reliable delivery from convenient warehouses in l.c.l. or l.t.l. quantities.

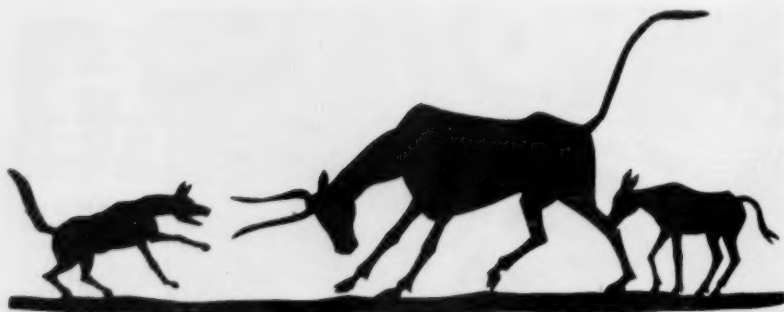
And this is only the beginning! Over 30 years' experience in synthetic rubber and other raw materials will bring even greater improvements. Why not start benefiting now by specifying PLIOFLEX? Write, on company letterhead, for a free copy of "PLIOFLEX Synthetic Rubbers," to:

Goodyear, Chemical Division,
Akron 16, Ohio

Chemigum, Pliobond, Plioflex, Pliolite, Plio-Tuf, Pliovic—T.M.'s
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...naturally protective

It's second nature for manufacturers to protect themselves by using modern developments and opportunities to secure better materials at lower cost. It will pay you to figure how much you can save by using **TEXAS 109**, the new Sid Richardson Carbon Co. super abrasion channel black.

TEXAS 109 gives the compounder many plus features in Butyl Rubber:

- More cures from air bags*
- Smoother liner stocks for tubeless tires*
- Better wire and cable covering*
- Just better performance*

Write for the new **TEXAS 109** brochure.

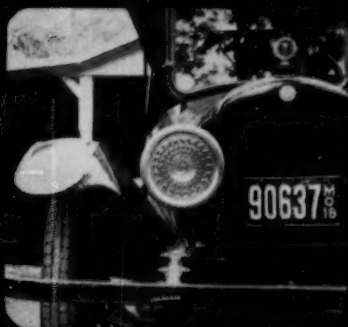


Sid Richardson
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How long did it take . . . to get from here . . . to here?



Answer: 27 years

Before electric headlights were introduced in 1913, night driving by feeble, undependable light was a risky venture. Further research led to today's high-performance sealed beam lights which became standard equipment on 1940 cars.

At the same time, the rubber industry was developing new and better ways to make rubber work harder. Partner in this development is Monsanto with its group of high-performance rubber chemicals which have done much to improve tires and other rubber products.

For example, Monsanto San-

tocure was the first commercially produced sulfenamide-type accelerator and with Santocure NS is considered a standard of the rubber industry. Santocure NS has similar behavior in compounded rubbers as Santocure. Its excellent delayed action gives greater freedom from scorch. The amount of Santocure NS can generally be reduced about 10% because of its greater strength.

Write today, for your copy of catalog "Chemicals for the Rubber Industry," to **MONSANTO CHEMICAL COMPANY**, Rubber Chemicals Dept., 920 Brown Street, Akron 11, Ohio.

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ANTIOXIDANTS

Flectal® H
Santoflex® DD
Santoflex 75
Santoflex AW
Santowhite® Crystals
Santowhite MK
Santowhite L
Santowhite Powder

MERCAPTO ACCELERATORS

Santocure® NS
Santocure
El-Sixty®
Mertax (Purified Thiotax)
Thiotax® (2-Mercapto-benzothiazole)
Thiofide® (2,2'-dithiobis (benzothiazole))
Thiofide S (Seed Form)

ALDEHYDE AMINE ACCELERATORS

A-32
A-100
SPECIAL MATERIALS
Thiocarbonyl ("A-1")
Santovar®-A
Sulfasol® R
Insoluble Sulfur "60"

ULTRA ACCELERATORS FOR LATEX, ETC.

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CHEMICALS—PLASTICS

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WHICH SERVES MANKIND

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Diphenylguanidine (D.P.G.)
Guantal®

COLORS

REODORANTS

Reg. U. S. Pat. Off.



Diary of an old shoe

*“Walked, walked, walked—on pavement and dirt—
month after month—mile after mile, rain or shine . . .”*

But this shoe could take it! It is one of millions of shoes that have the modern type of rubber sole reinforced by the incorporation of high styrene resins and plasticized with low cost **PANAREZ** hydrocarbon resins.

PANAREZ resins are tack producing agents and rubber softeners which make definite improvements in “flex crack”, abrasion and tear resistance, tensile strength, and aging properties. At the same time, **PANAREZ** resins permit the use of larger than normal quantities of filler without sacrificing quality. This has resulted in important reductions in raw material costs.

PANAREZ resins, derived from petroleum, act excellently as polymeric plasticizers. They provide excellent color and color stability. They have low specific gravity. They are particularly useful in GRS rubbers where improvements in processability and stock physicals are desired—at a simultaneously reduced cost.

Whether you compound or use rubber for shoe soles, wire covering, floor tiles, tires, hose, insulators or some other products, we welcome the opportunity to work confidentially with you on your particular problem. Readily available in various color grades and unlimited quantities, **PANAREZ** resins offer the compounder a completely reliable, low cost raw material.

For full information write or wire Dept. RC.



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PANAPOL
Hydrocarbon drying oils

PANASOL
Aromatic solvents



Stretch the life of rubber

with nonstaining *Wing-Stay S*

STOPPING one of rubber's arch enemies — oxidation — has long been a problem. New and better antioxidants and methods of evaluating them are under constant development.

One such method is the "creep test" wherein a rubber ring is placed under constant tension and heat and its stress decay periodically measured. It is in this test that PLIOFLEX 1502, a "cold" rubber protected with WING-STAY S, exhibits up to 15 times the age-resistance of the same unprotected rubber and up to three times that of similar rubbers containing another type of nonstaining antioxidant.

WING-STAY S is a liquid phenol-styrene copolymer. It specifically and effectively retards the detrimental action of oxygen. It is easily incorporated and highly resistant to heat, sunlight and extraction by water. It protects against degradation without odor, migration or discoloration. For details on PLIOFLEX—Goodyear Synthetic Rubber protected with WING-STAY S—or WING-STAY S alone, write to: Goodyear, Chemical Division, Akron 16, Ohio.



Chemigum, Pliobond, Plioflex, Pliolite, Plio-Tuf, Pliovic, Wing-Stay—T. M.'s The Goodyear Tire & Rubber Company, Akron, Ohio
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Deserves**

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DEPENDABLE IN PERFORMANCE... UNIFORM IN QUALITY

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Accelerator 808	Thionex
Accelerator 833	Thionex Grains
Butyl Accelerator 21	Thiuram E
DOTQ	Thiuram M
MBT	Thiuram M Grains
MBTS	Zenite
NA-22	Zenite A
Permalux	Zenite Special
Polyac	

ANTIOXIDANTS

Akroflex C	Neozone A
Akroflex CD	Neozone D
Antox	Permalux
	Thermoflex A

AQUAREXES

Aquarex L	Aquarex ME
Aquarex D	Aquarex NS
Aquarex G	Aquarex SMO
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BLOWING AGENTS

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RUBBER DISPERSED COLORS	RUBBER DISPERSED COLORS
Rubber Red PBD	Rubber Green GSD
Rubber Red ZBD	Rubber Blue PCD
Rubber Yellow GD	Rubber Blue GD
Rubber Green FD	Rubber Orange OD

ORGANIC ISOCYANATES

Hylone™M	Hylone™M-50
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PEPTIZING AGENTS

RPA No. 2	RPA No. 5
RPA No. 3	RPA No. 6
RPA No. 3 Concentrated	

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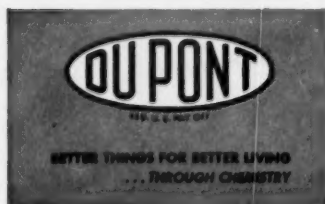
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Barak—Accelerator activator
Copper Inhibitor X-872-L—Inhibits
catalytic action of copper on elastomers
ELA—Elastomer lubricating agent
Heliozone—Sun-checking inhibitor
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MBT (Mercaptobenzothiazole)
MBT-XXX (Specially Refined—Odorless)
MBTS (Benzothiazylsulfide)
NOBS* No. 1 Accelerator
NOBS* SPECIAL Accelerator

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DPG (Diphenylguanidine)
DOTG (Diorthotolylguanidine)
Accelerator 49

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Antioxidant 2246®
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PEPTIZER

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RETARDER

Retarder PD

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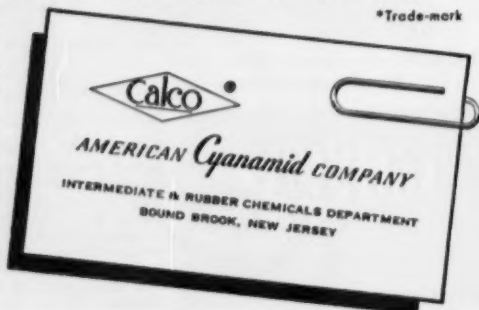
Rubber Makers' Grades



—with further significant research achievements still to come!

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CHANNEL BLACKS

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... here's a recipe that
will delight you!

*To Satisfy Your
Epicurean Taste
for*

**EASE OF PROCESSING
HIGH HARDNESS
ABRASION RESISTANCE**

*at low cost—
specify*

**NEVILLE
LX-685, 135**

SLAB SOLE COMPOUND

	Parts by Weight
GR-S, 1006	90
High Styrene Resin	10
NEVILLE LX-685, 135	12
Antioxidant	1
Calcium Silicate	50
Hard Clay	200
Zinc Oxide	5
Process Oil	5
Mold Lubricant	2.5
Stearic Acid	1.5
Benzothiazyl Disulfide	1.5
Zinc Dimethyl Dithiocarbamate	0.5
Rubbermakers Sulfur	4
Total	383.0

For extremely high hardness, approximately 5 parts of phenolic resin may be added.

Cure: 6 minutes at 310°F.

Specific Gravity: 1.66

Hardness, Shore A: 96

Color: Light Brown

Mold Release: Good

Hot Tear Resistance: Good

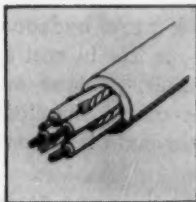
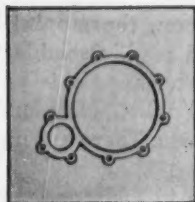
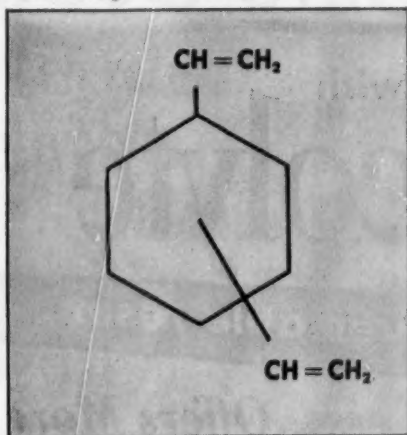
Cost per pound (estimated): \$.092

NEVILLE CHEMICAL CO.
PITTSBURGH 25, PA.

Plants at Neville Island, Pa., and Anaheim, Cal.

KOPPERS DIVINYLBENZENE . . .

reactive vinyl monomer • chemical intermediate



● Divinylbenzene (DVB) is a clear, mobile liquid. A highly reactive bi-functional monomer, it is of interest as a chemical intermediate and as a cross-linking agent for various polymers. DVB is useful for the production of copolymers such as synthetic ion-exchange resins, potting and laminating resins, modified drying oils and alkyl resins, and synthetic rubber.

Divinylbenzene is available in two grades:

DIVINYLBENZENE 50-60%—composed of the isomers of divinylbenzene and ethylvinylbenzene and some diethylbenzene. Particularly useful for applications requiring a

high proportion of reactive components.

DIVINYLBENZENE 20-25%—composed of the isomers of divinylbenzene and ethylvinylbenzene together with some styrene monomer, diethylbenzenes, toluene, benzene, and ethylbenzene. Especially useful in the production of Super Processing GR-S chemical rubbers, styrenated drying oils, and other products in which limited amounts of non-polymerizable compounds are not objectionable.

For further information on the properties, reactions, and applications of Divinylbenzene, write to:

KOPPERS COMPANY, INC.

Chemical Division, Dept. RCT-85, Pittsburgh 19, Pennsylvania



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Piccolyte

the versatile resin



Costs Less...Offers More!

Piccolyte—a pure hydrocarbon, thermoplastic terpene resin—is low in cost and readily soluble in low-cost naphthas, pentane and hexane. It is pale and stable in color, chemically inert, compatible with many other materials, non-toxic. There are nine melting points.

Piccolyte has the same carbon to hydrogen ratio as plantation rubber, and has excellent tack-producing properties. Ideal for rubber tile and other products where light colors and tints are demanded.

Use Piccolyte to keep your costs down without sacrificing in any way the quality of your products. Piccolyte costs less per pound today than practically all other resins, yet offers the maximum in quality and service.

Write for data booklet, and a free sample of PICCOLYTE. Give intended use, so we can send sample of appropriate grade.

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For Accelerators, Activators, Anti-Oxidants and Special Rubber Chemicals

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Write, on your letterhead, for technical data or assistance with any Naugatuck product.

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Naugatuck Chemical

Division of United States Rubber Company
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FOR TOUGHER, LONGER MILEAGE TUBELESS TIRES THAT DON'T SQUEAL...USE CIRCOSOL-2XH

Taking the objectionable squeal out of the new tubeless tires—without sacrificing abrasion resistance or toughness—is a problem in tread compounding as well as tread design. Tread design, of course, is somebody else's problem. But Sun's Circosol-2XH will solve your compounding problem.

The unique properties of Sun's Circosol-2XH are due to its scientifically controlled balance of naphthenic and aromatic hydrocarbons. By using Circosol-2XH in your tread stock, you can get a tubeless tire with high abrasion resistance, high flex-crack resistance, long mileage...and most im-

portant, it will be quiet running.

The cost of these extra advantages of Circosol-2XH is low. Enough Circosol-2XH for an 8.00 x 15 size, 100 level tire costs less than 2¢ more than the cheapest softener you can possibly buy.

Get the full story on both the advantages and the new low price of Circosol-2XH from your Sun representative...or write at once to SUN OIL COMPANY, Philadelphia 3, Pa., Dept. RC-7.



INDUSTRIAL PRODUCTS DEPARTMENT

SUN OIL COMPANY Philadelphia 3, Pa.

IN CANADA: SUN OIL COMPANY, LTD., TORONTO AND MONTREAL

JULY-SEPTEMBER • 1955

VOLUME XXVIII

• NUMBER THREE

RUBBER CHEMISTRY

AND TECHNOLOGY

PUBLISHED QUARTERLY BY THE
DIVISION OF RUBBER CHEMISTRY
OF THE AMERICAN CHEMICAL SOCIETY



CARBON BLACKS

for RUBBER COMPOUNDING

ISAF (Intermediate Super Abrasion Furnace)

STATEX®125

HAF (High Abrasion Furnace)

STATEX-R

MPC (Medium Processing Channel)

STANDARD MICRONEX®

EPC (Easy Processing Channel)

MICRONEX W-6

FF (Fine Furnace)

STATEX-B

FEF (Fast Extruding Furnace)

STATEX-M

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RUBBER CHEMISTRY AND TECHNOLOGY

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CONTENTS

General Section

	PAGE
Officers.....	iii
Future Meetings.....	vi
New Books and Other Publications.....	vi

Papers

The Thermal Effect in the Elongation and Relaxation of Rubber. J. P. EHRLICH AND CH. G. BOISSONAS.....	675
A Study of the Laws of Deformation of Loaded Elastomers. M. M. REZNIKOVSKI, L. S. PRISS, AND B. A. DOGADKIN.....	684
Experimental Determination of the Dynamic Viscosity and Elasticity and also the Relaxation Time Spectrum of Rubber. III. WERNER KUHN AND OTTMAR KÜNZLE.....	694
Testing of Rubber for Its Low-Temperature Stability by Measurement of the Loss of Elasticity. G. M. BARTENEV, S. B. RATNER, N. M. NOVIKOVA, AND R. S. KONENKOV.....	711
Thermodynamics of Crystallization in High Polymers. Natural Rubber. DONALD E. ROBERTS AND LEO MANDELKERN.....	718
X-Ray Investigation of the Amorphous State of Rubber. V. I. KASATOCHKIN AND B. V. LUKIN.....	728
Molecular Weights of Emulsion Polydienes. MAURICE MORTON.....	732
Degradation of High Polymers. Scission Reactions in the Oxidation of GR-S in Solution. I. Experimental Part. (MME.) J. CORTYL-LACAU.....	746
Infrared Study of the Oxidation of Elastomers. J. E. FIELD, D. E. WOODFORD, AND S. D. GEHMAN.....	770
The Role of Oxygen in the Vulcanization of Natural Rubber. A. S. KUZMINSKI AND V. F. CHERTKOVA.....	785
The Protection of Rubbers Against Ozone Cracking. Y. S. ZUEV.....	788
Joint Influence of Free and Combined Sulfur and of <i>N</i> -Phenyl-2-Naphthylamine on the Oxidation of Vulcanized Rubber. A. S. KUZMINSKI AND S. I. BASS.....	793
Reaction of a Thiuram and Sulfur. G. A. BLOKH AND L. P. SAZONOVA.....	804
Studies of the Mechanism of the Mastication of Rubber. VIII. The Reaction of Natural Rubber with 3,5-Dibromobenzoyl Peroxide. MINORU IMOTO AND SHIGERU KIRIYAMA.....	808

A Study of Permeability to Gases. Mixtures of Natural Rubber and Other Elastomers. JEAN BARBIER.....	814
The Effect of Fillers on the Permeability of Rubber to Gases. G. J. VAN AMERONGEN.....	821
Importance of the Polar Component of Mixed Fluids in the Swelling of Vulcanizates. I. N. ERMOLENKO, M. I. MAZEL, AND N. F. ERMOLENKO.....	833
Thermodynamics of the Swelling of Natural Rubber and Sodium-Butadiene Rubber in Binary Mixtures. G. L. STAROBINETS AND KH. M. ALEKSANDROVICH.....	838
Vulcanization of Crepe Rubber by Sulfur Monochloride. II. The Dilatometric Method. J. GLAZER.....	850
The Curing of Silicone Rubber with Benzoyl Peroxide. A. M. BUECHE.....	865
Performance of Carbon Blacks. Influence of Surface Roughness and Porosity. E. M. DANNENBERG AND B. B. S. T. BOONSTRA.....	878
Structure and Dielectric Properties of Rubber Mixtures Containing Carbon Black. B. DOGADKIN AND A. LUKOMSKAYA.....	891
Promoters for the Reaction of Rubber with Carbon Black. KENNETH W. DOAK, GEORGE H. GANZHORN, AND BERNARD C. BARTON.....	895
The Abrasion of Rubber. A. SCHALLAMACH.....	906
Mooney Viscosity Changes in Freshly Prepared Raw Natural Rubber. R. I. WOOD.....	917
Evidence for a Hydrochlorination Retarder within Natural-Rubber Latex Particles. MANFRED GORDON AND JAMES S. TAYLOR.....	918
Structure and Rheological Properties of Hevea Latex Gels. A. J. DE VRIES AND M. VAN DEN TEMPEL.....	922
Solubility of Zinc Oxide in Preserved Hevea Latex. M. VAN DEN TEMPEL.....	927

RUBBER CHEMISTRY AND TECHNOLOGY

RUBBER CHEMISTRY AND TECHNOLOGY is published quarterly under the supervision of the Editor, representing the Division of Rubber Chemistry of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

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FUTURE MEETINGS

The Division of Rubber Chemistry of the American Chemical Society is scheduled to hold meetings in the following cities in 1955, 1956, and 1957.

Meeting	City	Hotel	Date
1955 Spring	Detroit*	Sheraton-Cadillac	May 4-6
1955 Fall	Philadelphia*	Bellevue-Stratford	November 2-4
1956 Spring	Cleveland*	Cleveland	May 16-18
1956 Fall	Atlantic City	—	September 19-21
1957 Spring	Montreal*	Sheraton-Mt. Royal	May 15-17
1957 Fall	New York	—	September 11-13

* The meeting will be held independent of, and at a different time from, the corresponding spring or fall meeting of the American Chemical Society.

NEW BOOKS AND OTHER PUBLICATIONS

EMULSION POLYMERIZATION. By Frank A. Bovey, I. M. Kolthoff, Avrom I. Medalia, and Edward J. Meehan. Published by Interscience Publishers, Inc., 250 Fifth Ave., New York 1, N. Y. 6 × 9 in. 446 pp. \$12.50.—Issued as Volume IX in the series of monographs on the chemistry, physics, and technology of high polymeric substances published under the title of "High Polymers", this work concerns itself with emulsion polymerization.

The present book is a broad survey and systematic interpretation of the various aspects of the kinetics of emulsion polymerization and of the properties of the intermediate and final products. It is by no means a research report, but rather a systematic treatment of the entire problem and the results achieved to date. It is, therefore, not only a record of past performance, but also a stimulus to research and development beyond the present stage of the art.

There are eleven chapters: (1) Historical Background and General Considerations; (2) Nature of Free-Radical Polymerization; (3) Initiating Systems; (4) Chain Transfer Agents; (5) Solubilization in Detergent Micelles; (6) Kinetics of Emulsion Polymerization; (7) Inhibition and Retardation of Polymerization; (8) Copolymerization in Emulsion Systems; (9) Experimental Methods in Emulsion Polymerization; (10) The Standard GR-S Recipe; (11) Activated Recipes. [From the *Rubber Age* of New York.]

SOME ASPECTS OF THE CRYSTALLIZATION OF HIGH POLYMERS. By G. Schuur. (Communication No. 276.) Published by Rubber-Stichting, Oostingel 178, Delft, Netherlands. 6½ × 9½ in. 82 pp. Hfl. 5 (approximately \$2.00).—

According to the author, a high polymer can crystallize in two different manners: On quenching and annealing a polymer crystallizes without the formation of spherulites. Under normal conditions, however, spherulites are formed. This booklet deals chiefly with the formation and structure of the spherulites, and a theory is proposed, according to which the spherulites are the result of an internal flow of the material prior to crystallization. Experimental evidence is shown that individual crystallites are non-existent within the spherulites, in contradiction to the well-known micellar theory. The crystalline material would be continuous also in oriented fibers and stretched rubbers. The stress-strain curves are discussed on this basis. Finally, some other aspects of the crystallization, such as the crystallization curves, the fact that polymers always crystallize under non-equilibrium conditions, the melting behavior of natural rubber, and the crystallization of finely divided particles of polymers in emulsions are discussed in the light of these new concepts. There are 35 photographs and figures and 101 references, which contain most of the literature about spherulites in high polymers up to October 1954. [From the *Rubber Age* of New York.]

MECHANISM OF POLYMER REACTIONS. By G. M. Burnett. Published by Interscience Publishers, Inc., 250 Fourth Ave., New York 1, N. Y. 6 × 9 in. 494 pp. \$11.00.—The decade which has passed since the publication of Mark and Raff's work on the theory and practice of high polymeric reactions has seen many dramatic advances in the field of high polymer chemistry. These advances are reflected in the present book, which constitutes a new edition of Volume III in the series of monographs on the chemistry, physics, and technology of high polymeric substances, but which has been issued as Volume IX in the series. The extensive growth of the subject has made it impossible to follow the pattern of the first edition, so the present book may be regarded as a completely new work.

The scope of the work is best indicated by the titles of its twelve chapters: (1) General Kinetics; (2) Experimental Methods; (3) Addition Radical Polymerization; (4) Kinetics of Radical Polymerization; (5) Gas Phase Polymerization; (6) Homogeneous Liquid-Phase Polymerization; (7) Rate Constants of Radical Polymerization Reactions; (8) Copolymerization; (9) Heterogeneous Liquid-Phase Polymerization; (10) Degradation of High Polymers; (11) Ionic Polymerization; (12) Condensation Polymerization. Author and subject indexes are included.

Referring to the wealth of data on the individual reactions making up the radical chain process in the bulk reaction which has appeared in the past several years, the author makes the point that the modifications brought about by the introduction of solvents are still not fully understood. He adds that it may well be that in this field much interesting and important information lies buried. [From the *Rubber Age* of New York.]

THE STORY OF THE TIRE. Goodyear Tire & Rubber Co., Akron, Ohio. 6 × 9 in. 64 pp.—To read this booklet is to get a cross-sectional view of the automobile and air ages, the rubber industry, tires, the Goodyear company, and the American business structure. The booklet traces the history of the rubber industry from its earliest historical references through the discovery of vulcanization to the present. The booklet discusses the development of synthetic rubber, outlines the development and use of tire fabrics, and gives a

step-by-step description of the manufacture of a tire. Research activities entered into by the company are described. This interesting booklet is illustrated by diagrammatic sketches and photographs. [From the *Rubber Age* of New York.]

MAN-MADE RUBBER AND THE MEN WHO MADE IT. By William S. Richardson. B. F. Goodrich Co., Akron, Ohio. $3\frac{1}{4} \times 7$ in. 28 pp.—In this interesting booklet, the author, president of the B. F. Goodrich Co., traces the progress of synthetic rubber during the past twenty-five years. While not intended to be a complete history, the booklet opens with the efforts of American chemists to produce man-made rubber nearly fifty years ago and covers the remarkable accomplishments in this field since then. The behind-the-scene efforts to establish the rubber-making facilities in this country in time to avoid disaster during World War II are dealt with step-by-step. In the author's opinion, American competitive enterprise, the government's stockpiling and synthetic rubber programs, "and the cooperation of millions of American citizens in the conservation of rubber won America's victory in rubber". [From the *Rubber Age* of New York.]

RUBBER'S RETURN TO THE WESTERN HEMISPHERE. Public Relations Department, Goodyear Tire & Rubber Co., Akron, Ohio. 6×9 in. 24 pp.—This booklet recounts the history of the rubber plantation industry from its inception in the Western Hemisphere to its transfer and growth in the East to the current establishment of a rubber plantation industry in Latin America. It is concluded that for our national security and for the combined welfare of the sister republics of the Western Hemisphere, a large-scale rubber plantation industry is both economically possible and desirable. In this regard, the booklet tells of the establishment of rubber plantations by Goodyear in Costa Rica. A series of photographs illustrate scenes on the plantations. [From the *Rubber Age* of New York.]

REPORT OF THE MISSION OF ENQUIRY INTO THE RUBBER INDUSTRY OF MALAYA. Available from the British Information Services, 30 Rockefeller Plaza, New York 20, N. Y. $6\frac{1}{2} \times 9\frac{1}{2}$ in. 76 pp. \$1.15.—This report is the work of a body independent of the Malayan Government and of the rubber producing industry. It was charged with making an impartial investigation into certain aspects of the competitive position of the rubber producing industry. This investigation was completed in August, 1954, and the results and recommendations are contained in this published report. The report covers such phases as the future of natural rubber, the Malayan rubber industry, costs of estate rubber, the case for replanting, taxation, maintenance of existing capital, marketing and processing of small holders' rubber, research and advisory work, and unemployment in the rubber producing industry. It poses three vital questions: (1) Is it possible for Malaya to increase its present output of rubber? (2) Must Malaya be content to maintain its present output of rubber? (3) Must Malaya resign itself to a gradual decline and eventual decay? The Commission's answer to these questions is that, in spite of the age of her trees and the competition of synthetic rubber, Malaya can continue to prosper and her output of rubber can be increased, providing vigorous and united action is taken on an expanded replanting program. The report contains a wealth of information for those directly or indirectly con-

cerned with the future of the natural rubber industry. [From the *Rubber Age* of New York.]

GAS PERMEABILITY OF RUBBER COMPOUNDS. (Technical Service Laboratory Bulletin No. GD-11.) Research Laboratories, Godfrey L. Cabot, Inc., Cambridge, Mass. $8\frac{1}{2} \times 11$ in. 4 pp.—This condensed survey of the available literature on permeability should be of interest in connection with the rapidly expanding use of tubeless tires. Two interesting tables are presented: In Table I, compiled from the literature, values for the permeability constant are given for oxygen and nitrogen in various polymers and at different temperatures; Table II shows permeability constants ($Q \times 10^{-8}$) for compounds of various fillers in natural rubber. A listing of literature of interest is appended. [From the *Rubber Age* of New York.]

ADHESION AND ADHESIVES—FUNDAMENTALS AND PRACTICE. Edited by F. Clark, John E. Rutzler, and Robert Savage. John Wiley & Sons, Inc., New York, N. Y. Cloth, $8\frac{1}{2} \times 11\frac{1}{4}$ inches, 229 pages. Price, \$9.75.—The volume consists of edited papers read at a symposium sponsored by Case Institute of Technology, Cleveland, April 24-25, 1952, and the contributions and discussions from England's Society of Chemical Industry's conference, held in London, April 22-24, 1952. The purpose of both conferences was to bridge the gap between new product research and the development of better adhesives, with the emphasis on theory. The 43 papers cover such topics as joint strength, solid-solid interfaces, fluids, and molecular and intermolecular forces. Fields covered include plastics; rubber, wood, paper, glass, roads, films, aircraft, metals, and textiles. This book is illustrated with photographs, tables, and graphs. [From the *Rubber World*.]

SYMPOSIUM ON CARBON BLACKS READ AT THE FALL MEETING OF THE SWEDISH INSTITUTION OF RUBBER TECHNOLOGY, NOVEMBER 26, 1954. Sveriges Gummitekniska Förening, Stockholm, Sweden. About 130 pages, mimeographed. All but one of the eight papers presented at the above meeting, which have been collected together in the present publication, are in English. Papers by I. Drogin, United Carbon Co.; C. W. Sweitzer, Columbian Carbon Co.; L. D. Carver, Witco Chemical, and R. A. Reinke, Witco Continental Carbon; H. J. Collyer, Cabot Carbon, Ltd.; and J. Willums, Phillips Chemical Co., have been reported on in *Rubber World*, the first on page 514 of the January, 1955, issue, and the remaining four, on page 648 of the February, 1955, issue. "Influence of Carbon Black on Oxidation, Hysteresis, and Wear of Rubber", was discussed by G. J. van Amerongen, of Rubber Stichting, Delft, Netherlands; while N. C. H. Humphreys spoke on "Technical and Economic Aspects of Blends of Carbon Blacks". The single paper in German, by H. Westlinning, deals with investigations in the laboratories of Degussa Co. on the behavior of active carbon during compounding and the static and dynamic properties of the rubber vulcanizates. [From the *Rubber World*.]

PROCEEDINGS OF THE INTERNATIONAL SYMPOSIUM ON ABRASION AND WEAR. (Communication No. 211.) Rubber-Stichting, Delft, Holland. $9 \times 11\frac{1}{2}$ in. 66 pp.—This attractive publication contains a report of the proceedings of the International Conference on Abrasion and Wear, held at Delft, Holland, on November 14 and 15, 1951, under the sponsorship of the Rubber-Stichting.

The ten papers which were presented at that time appear here in printed form. Also published are the discussions which followed the presentation of each paper. The publication is liberally illustrated with photographs, charts, and graphs. [From the *Rubber Age* of New York.]

PROCEEDINGS OF THE JOINT ARMY-NAVY-AIR FORCE CONFERENCE ON ELASTOMER RESEARCH AND DEVELOPMENT. (Publication No. 30.) Published by the National Academy of Sciences, Washington, D. C. $8 \times 10\frac{1}{2}$ in. 148 pp.—Since 1950, the three military services of the government have participated at approximately two-year intervals in joint conferences on elastomer research and development. The current publication covers the joint conference on January 12-13, 1954. About 250 rubber technologists and military officials participate in these conferences, which are credited with achieving definite improvements in the multitudinous rubber products utilized by the armed services.

The conference covered in this report was divided into two sessions, the first concerned with the progress and status of elastomers from the viewpoints of the Army, Navy, Air Force, Office of Synthetic Rubber and Industry, and the second devoted to elastomer deterioration research, the replacement of natural rubber, and some other areas of elastomer research. Pertinent papers on the various subjects were presented by outstanding authorities, all of which are reproduced in full in the Proceedings.

Among the papers presented at the session devoted to elastomer deterioration research were the following: Aging Studies on Commercial Vulcanizates (L. R. Pollack); The Continuous Measurement of Atmospheric Ozone by an Automatic Photoelectric Method (R. Stair, T. C. Bagg, and R. G. Johnston); Methods for the Evaluation of Chemical Protectants as Inhibitors of Ozone-Induced Degradation of GR-S (A. D. Delman, B. B. Simms, and A. R. Allison); Replication Methods for the Investigation of Ozone Surface Effects on Elastomer Compounds (A. Reisman and A. D. Delman); Radioisotope-Tracer Techniques for the Quantitative Measurement of Surface-Cracking in Elastomers (J. L. Kalinsky and T. A. Werkenthin); Determination of Loss of Plasticizers in Vulcanizates by Volatilization (J. Oser, A. E. Barrett, and R. E. Morris).

Space does not permit the listing of all the papers and authors, but the session on replacement of natural rubber covered such topics as the development of high-synthetic-content truck tires, development of a tire tester, the synthesis of oriented high polymers, biosynthesis of rubber, and synthesis of rubber by microorganisms. Among subjects treated at the session on other elastomer research were fluorine-containing elastomers, compounding and processing of Poly-FBA, flow properties of liquid polysulfide compounds, and problems in the development of oil-resistant arctic rubber.

The inclusion of all of this material, plus the various progress reports submitted by the different services, makes these Proceedings a valuable addition to the technical literature. Although slanted to the military point of view, there is a wealth of information of direct interest for industrial rubber goods in general. [From the *Rubber Age* of New York.]

ASTM STANDARDS ON RUBBER PRODUCTS (WITH RELATED INFORMATION). December, 1954. Prepared by ASTM Committee D-11 on Rubber and Rubber-Like Materials. Published by American Society for Testing Materials,

1916 Race St., Philadelphia, Pa. Price, \$5.50; ASTM members, \$4.25.—THIS special compilation of standards gives in convenient form all of the widely used standard methods of test and specifications on rubber developed by Committee D-11, including additions and revisions made since the last issue of this book in December, 1952. There is an appendix covering Proposed Methods of Testing Rubber Thread and regulations governing Committee D-11. [From the *Rubber World*.]

1954 SUPPLEMENT TO BOOK OF ASTM STANDARDS INCLUDING TENTATIVES —Part 6: Rubber, Plastics, Electrical Insulation. American Society for Testing Materials, Philadelphia, Pa. Paper cover, 532 pages. Price, \$3.50.—This supplement to the original 1952 edition and to the 1953 supplement includes 66 standards covering such rubber products as automotive and aeronautical rubber, packing and gasket material, hose, latex foam, and expanded cellular rubber; plastics specifications, physical properties, analytical methods, and definitions; and electrical insulating materials and electrical tests. [From the *Rubber World*.]



THE THERMAL EFFECT IN THE ELONGATION AND RELAXATION OF RUBBER *

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When rubber is stretched, its temperature rises, and when the tension is released and the rubber relaxes, it becomes cooler. This phenomenon is known as the heat effect or the Gough-Joule effect, from the names of the authors who first described the phenomenon¹. This heat effect depends on two different factors. On the one hand, the work of extension is transformed into heat, and inversely, heat is consumed in the work of relaxation. In addition to this, if the elongation is considerable, the stretching induces the formation of a crystalline phase in the mass of rubber, and this is accompanied by the evolution of latent heat of crystallization. Correspondingly, during relaxation, the disappearance of the crystalline phase involves the absorption of the latent heat of fusion, as a result of which the rubber becomes cooler.

The heat effect in rubber has already been described in numerous works, which are cited in particular in publications by Davis and Blake² and Treloar³. Gleichentheil and Neumann⁴ alone studied the heat evolved in the isothermal extension of a sample of rubber immersed in a mercury calorimeter. Other investigators, including Chauveau⁵, Williams⁶, Ariano⁷, Boone and Newmann⁸, Ornstein, Wouda, and Eymer⁹, and Dart, Anthony, and Guth¹⁰, employed a direct method, which comprised following, by means of a thermoelectric couple, the changes of temperature in a rubber sample subjected to sudden stretching and relaxation. These investigators assumed that, under such conditions, the heat effect is so rapid that it can be regarded as an adiabatic transformation, i.e., the heat absorbed by the rubber from the surrounding air or lost by the rubber to the surrounding air is assumed to be negligible.

Dart, Anthony, and Guth¹⁰ in experiments with synthetic rubber proved that the rise of temperature after extension is greater than the fall of temperature during subsequent relaxation. They state further, without offering any explanation, that the rise of temperature during extension is less than the fall of temperature accompanying relaxation, whereas the corresponding heat effects are the opposite. This paradox can be explained, according to Boissonas¹¹, by the fact that heat continues to be evolved for a long time after stretching whereas relaxation is accompanied by a more rapid thermal phenomenon.

It would seem, therefore, in view of the results obtained up to the present time, that in any study of the heat effect in rubber, it is necessary not only to take account of the rise of temperature during the first few seconds after stretching but also to follow, during an extended length of time, with proper corrections, the rise of temperature which occurs in the rubber sample if the extension has been adiabatic. This is the problem which was undertaken in the present work.

* Translated from RUBBER CHEMISTRY AND TECHNOLOGY from *Helvetica Chimica Acta*, Vol. 38, No. 1, pages 125-134, January 1955.

We shall see later that an empirical correction for the heat losses can be made with fairly good precision during a period of about ten minutes. Later, a method was employed which was based on the temperature lowering resulting from the relaxation, as a function of the time that the rubber was kept elongated, and which was applied for times up to twenty hours. In addition, by measurements of the elongation of the sample during extension and relaxation it is possible to establish the balance of the thermodynamic cycle.

APPARATUS AND EQUIPMENT

The frame (Figure 1) on which the rubber sample is stretched from its two ends at the same time, while its center section does not move, is protected by a copper case, the function of which is to minimize air currents. Its temperature,

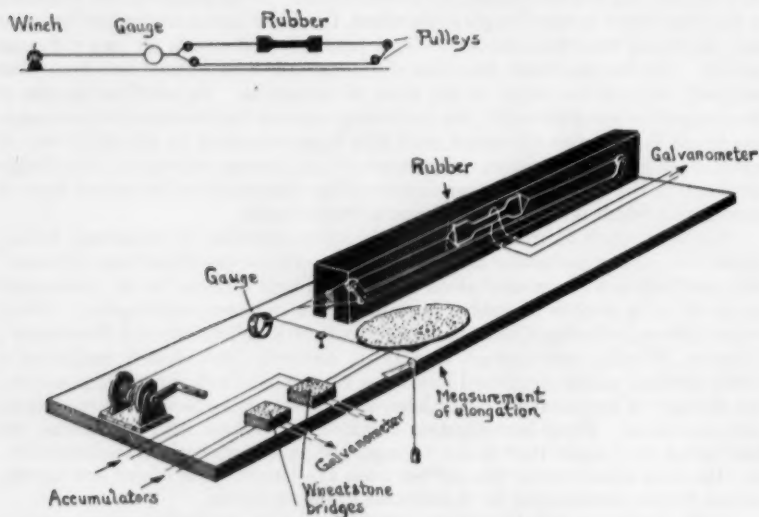


FIG. 1.—Diagrammatic assembly of apparatus for stretching.

which is practically constant and equal to that of the room, serves as a reference temperature. The rubber sample is in the form of a strip died out from a sheet and of such shape that, folded upon itself and cemented, it has the form of a dumbbell. The middle rectilinear section of this test-specimen holds one of the junctions of a constantan-copper thermoelectric couple, the other junction of which is located on the copper case. The couple is connected with a mirror galvanometer¹², the deflection of which is read on a graduated scale. A deflection of approximately 8 cm. represents a temperature difference of one degree between the junctions. Two marks, 4 cm. apart, on the test-specimen serve to measure the percentage elongation.

The stress applied to the test-specimen is measured by means of a Philips strain gauge (G.M. 4472) fastened to a ring of tempered steel (diameter 7 cm., length 3 cm., thickness 0.8 mm.). Deformation of this ring, attached to an extension cord, changes the electric resistance of the gauge, which comprises

part of a Wheatstone bridge connected with a galvanometer¹². The deflections of the latter are recorded on a rotating drum carrying photographic paper.

The elongation of the test-specimen is recorded in the same way by a second galvanometer¹². A nylon thread connected with the stretching cord activates an auxiliary disk, with circular variable resistance, which forms part of a Wheatstone bridge connected with a galvanometer. With this assembly, there are recorded, on the same photographic paper, measurements of the applied stress and the elongation, from which the work of extension and the work of relaxation can be determined. Before each operation, the system must be standardized by means of weights. In the present work, the test-specimens were stretched and relaxed at rates as constant as possible in 4 to 5 seconds.

CORRECTION OF HEAT LOSSES

With the apparatus described, it is possible to determine, as a function of time, the temperature difference between the copper case (at constant temperature) and the rubber test-specimen. From these data, the next step is to determine, for as long a period of time as possible, the temperature which the test-specimen would reach if it neither gave up heat to, or absorbed heat from, the surrounding medium, i.e., if the conditions of both stretching and relaxation were adiabatic.

Experiments show that, when a sample of rubber is heated by stretching, its heat loss into the surrounding air takes place chiefly by conduction and convection and only to a relatively small extent by radiation. This can be explained by the fact that the temperature difference between the sample and the surrounding space is only a few degrees. An attempt can, therefore, be made to apply the law of cooling of Newton:

$$d\theta/dt = -c\theta$$

where θ is the temperature difference, t is the time, and c is a constant. If t_0 is the initial time and t_n is some other time, the temperature drop of the sample resulting from heat loss during the time interval, $t_n - t_0$, is:

$$\Delta\theta = -c \int_{t_0}^{t_n} \theta dt$$

Integration can be made graphically by plotting the experimental values of θ as a function of t .

To determine c , a sample is held at a chosen percentage elongation and is heated by passing an electric current through a constantan wire embedded in zig-zag shape within the sample. After the heating is stopped, the cooling curve is recorded. According to Newton's law, when $\log \theta$ is plotted as a function of time, a straight line should be obtained, from the slope of which the value of c is obtained. Experiments show that c is not constant, but varies with θ , because of the fact that the air within the case becomes heated. Nevertheless, a study of this heating of the air surrounding the sample shows that it is of the same order of magnitude during extension and during heating in the determination of c , so that the values of c obtained experimentally for each value of θ can be used for the correction of heat losses.

In this way it can be proved¹¹ that, when a sample of natural rubber is stretched, heat continues to be evolved for some time (at least for ten minutes) after the stretching operation. On the contrary, during relaxation, heat is

evolved more rapidly, and the process is practically complete in one or two minutes.

The precision of the results is the greater, the smaller is the correction factor $\Delta\theta$. Since, during extension, evolution of heat is relatively slow, the correction for heat losses was applied to as long a period of time as possible. To this end, a sample was stretched at a temperature which, in the beginning, was lower than that of the room. In this way, the temperature of the sample after stretching should be close to that of the surrounding temperature. On the contrary, during relaxation, the heat effect is rapid, and therefore the results are fairly accurate, even when there is a considerable difference of temperature between that of the rubber sample and that of the surrounding medium. For this reason, relaxation was carried out with the initial temperature that of the room.

This method of operation necessitates preliminary cooling of the rubber sample, which can be effected by preliminary relaxation or by vaporization of ether on its surface. The same results were obtained by these two methods,

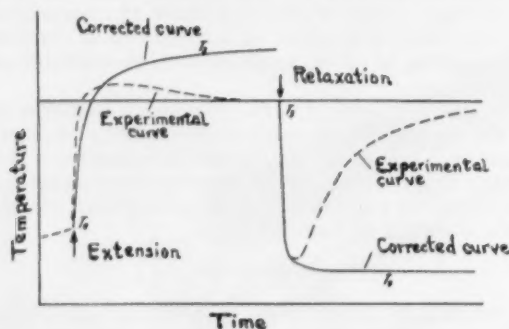


FIG. 2.

but the former was adopted in order to avoid any risk of changing the structure of the rubber because of swelling by the ether.

Under these conditions, the correction for heat losses can be applied with satisfactory precision for a period of ten minutes after the stretching operation, and thus heating of the rubber as a function of time can be followed.

As a means of control, the balance of an elongation-relaxation curve was established. Let w_e be the work expended in stretching the sample, w_d the work recovered during relaxation, T_1 the initial temperature, T_2 the temperature corrected to time t after extension, T_3 the temperature before relaxation, and T_4 the temperature corrected to the time t after relaxation (see Figure 2). For an adiabatic transformation, the increase of internal energy is equal to the work expended. We have, then, for extension:

$$E_{T_2} - E_{T_1} = w_e \quad (1)$$

and

$$E_{T_4} - E_{T_3} = -w_d \quad (2)$$

By addition of Equations (1) and (2):

$$E_{T_2} - E_{T_1} + E_{T_4} - E_{T_3} = w_e - w_d \quad (3)$$

If C_s represents the heat capacity of the sample in the stretched state and C_d is its heat capacity in the relaxed state, then:

$$E_{T_1} - E_{T_4} = C_d(T_1 - T_4) \quad (4)$$

and

$$E_{T_2} - E_{T_3} = C_s(T_2 - T_3) \quad (5)$$

whence, by substituting in Equation (3):

$$-C_d(T_1 - T_4) + C_s(T_2 - T_3) = w_s - w_d \quad (6)$$

From the work of Mayor and Boissonas¹³, one can deduce that, under the conditions of most of the experiments in the present work, for an elongation of 4.5 and a temperature difference of 6° C between the rubber and surrounding medium, C_s is approximately 10 per cent greater than C_d . This difference is reduced to 2 per cent when the elongation is 3.0. This estimation takes into account the variation of specific heat due, at the same time, to stretching the sample and to the temperature difference between the relaxed state and the elongated state.

Taking as a basis this variation of the specific heat, Equation (6) was verified for periods of time up to ten minutes after stretching, within an approximation closer than 5 per cent. This justifies the application of the method of correction which was applied. For periods of time greater than ten minutes, the following method was utilized.

The sample is stretched, then held at constant elongation for time t , and finally allowed to relax. The temperature drop, $T_3 - T_4$, due to relaxation can be determined with a precision of 2-3 per cent, because, as has already been pointed out, heat evolution is rapid during relaxation. By means of this $T_3 - T_4$ value, and knowing w_s and w_d on the one hand and the heat capacities C_s and C_d on the other hand, as well as T_1 , it is possible from Equation (6) to determine T_2 and, consequently, $T_2 - T_1$, i.e., the temperature rise at time t following stretching. However, the temperature differences, $T_1 - T_4$ and $T_2 - T_3$ in Equation (6) are relatively small, and so the $T_2 - T_1$ value which is found depends only slightly on the C_d and C_s values. Under these conditions, the following equation was used:

$$C[(T_2 - T_1) - (T_3 - T_4)] = w_s - w_d \quad (7)$$

where C is the heat capacity of the sample, which is assumed to be constant, irrespective of the elongation. For C , a mean value was chosen which corresponded to a specific heat of 0.45 cal.-g.⁻¹-degree⁻¹.

It should be noted that, after ten minutes, $w_s - w_d$ tends toward a practically constant value, for then the relaxation no longer has much influence. Accordingly, in what follows, we have applied the correction for heat losses up to the ten-minute interval and the temperature lowering during relaxation up to twenty hours. Beyond this time, it was found that there was a smaller lowering of the temperature during relaxation, probably because of plastic reconstruction.

RESULTS OF THE MEASUREMENTS

The measurements were carried out with three natural-rubber vulcanizates (Nos. 1, 2, and 3) and two synthetic-rubber vulcanizates (No. 4, Neoprene, and No. 5, Butyl rubber).

The following tabulation shows the characteristics of these five samples.

Sample No. 1 (Source: Lonstroff, Geneva). Ash content 5.5 per cent; total sulfur 1.8 per cent; specific gravity 0.9675 g. per cc.

Sample No. 2 (Source: French Rubber Institute, Paris). Composition: smoked sheet 100, sulfur 3.5, mercaptobenzothiazole 0.5, stearic acid 0.5, zinc oxide 6. Specific gravity 0.9878 g. per cc. Vulcanized 20 minutes at 140° C.

Sample No. 3 (Source: Neff & Specker, Zurich). Ash content 2.4 per cent; total sulfur 2.1 per cent; specific gravity 0.9513 g. per cc. Vulcanized 20 minutes at 140° C.

Sample No. 4 (Source: French Rubber Institute, Paris). Composition: Neoprene-W 100, magnesia 4, zinc oxide 5, stearic acid 0.5, Neozone-A 2, Permalux 0.5. Specific gravity 1.3161 g. per cc. Vulcanized 30 minutes at 143° C.

Sample No. 5 (Source: French Rubber Institute, Paris). Composition: Butyl rubber 100, tetramethylthiuram disulfide 1, benzothiazolyl disulfide 1, sulfur 2, stearic acid 0.5, zinc oxide 5. Specific gravity 0.9800 g. per cc. Vulcanized 30 minutes at 143° C.

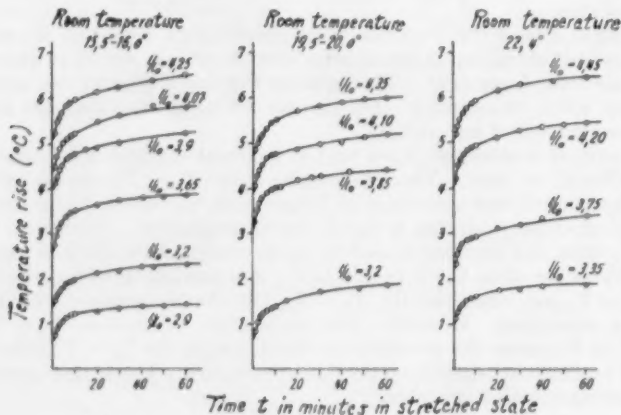


Fig. 3a

Fig. 3b

Fig. 3c

Sample No. 1

FIGS. 3a, 3b, AND 3c.—Sample no. 1. Temperature rise caused by stretching as a function of the time that the sample is stretched.

From these five samples, dumbbell specimens were died out, as described earlier in this work. The middle section was 1.5 cm. wide, 0.6-0.7 cm. thick, and 4 cm. long between bench-marks.

Figures 3, 4, 5, 6, and 7 show the temperature rises resulting from stretching as a function of the time that the sample is kept elongated. Each measurement is indicated by a small circle. Up to ten minutes, the points represent corrected values of the heat losses; for times longer than ten minutes, the points represent $T_2 - T_1$ values, derived from Equation (7).

INTERPRETATION OF THE RESULTS

A study of the graphs in Figures 3, 4, 5, 6, and 7 will show that the samples of natural rubber gave, when they were stretched, a heat effect which continued for a long time; in fact, at the end of an hour, the temperature rise had not

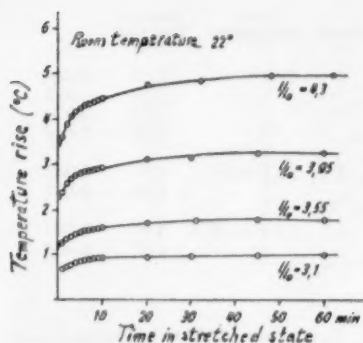


Fig. 4

Sample No. 2

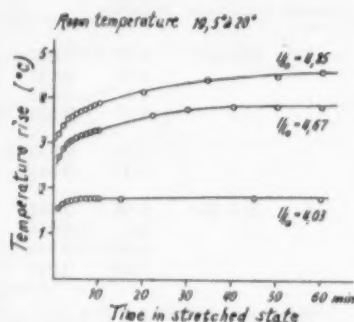


Fig. 5

Sample No. 3

FIG. 4 AND FIG. 5.—Samples nos. 2 and 3. Temperature rise caused by stretching as a function of the time that the sample is stretched.

come to an end. On the other hand, in the case of the samples of synthetic rubbers, the heat effect was manifest only during the first few minutes following stretching. This explains the divergencies pointed out by Dart, Anthony, and Guth¹⁰, and confirms the explanation of this phenomenon offered by Boissonas¹¹.

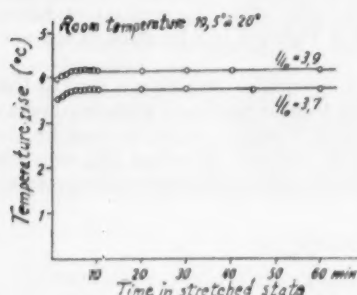


Fig. 6

Sample No. 4

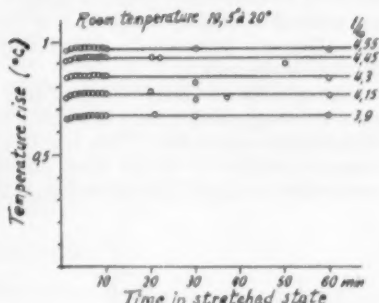


Fig. 7

Sample No. 5

FIG. 6 AND FIG. 7.—Samples nos. 4 and 5. Temperature rise caused by stretching as a function of the time that the sample is stretched.

The form of the curves showing the temperature as a function of the time for the natural-rubber samples (Figures 3, 4, and 5) can be expressed by the relation:

$$\theta/\theta_0 = 1 - e^{-Kt} \quad (8)$$

where K is a constant, θ is the temperature rise for a given time of extension, θ_0 is the temperature rise, extrapolated to an infinite period of time during extension, and t is the time that the particular sample remains in the stretched state.

However, this relation has been found to be valid only for times of extension longer than ten minutes. The K values derived from the curves of Figures 3, 4 and 5 are recorded in the following table.

Sample no.	Room temperature (°C)	Relative elongation (1/l ₀)	K	Sample no.	Room temperature (°C)	Relative elongation (1/l ₀)	K
1	15.5-16°	4.25	0.039	1	22.4°	4.45	0.030
		4.07	0.041			4.20	0.032
		3.9	0.035			3.75	0.039
		3.65	0.028			3.35	0.046
		3.2	0.035	2	21.7-22.1°	4.3	0.037
		2.9	0.041			3.95	0.037
1	19.5-20°	4.35	0.041	3	19.4-20.0°	4.85	0.039
		4.1	0.035			4.67	0.025
		3.85	0.041				
		3.2	0.046				

The mean value of K is 0.038 ± 0.005 . It was found that this value is only slightly dependent on the percentage elongation, of the type of vulcanizate, or of the temperature, at least within the temperature range of 15-22° C.

Thiessen and Wittstadt¹⁴ studied the double refraction of a sample of rubber as a function of the time that it was kept elongated. They obtained curves of the same form, and from these we have been able to derive values of K of the same order of magnitude as those given above.

In Figure 8, curves show the temperature rise due to stretching, and also the temperature drop accompanying relaxation, as functions of the percentage elongation, extrapolated to infinite time in the elongated state (θ_0 in Equation (8)). The heat effect depends greatly on the type of vulcanizate. Knowing the work of extension, the portion of the heat effect due to crystallization during stretching can be derived. This is shown in Figure 9 as a function of the percentage elongation.

Sample No. 5 (Butyl rubber) does not crystallize (see Figure 9). In this case, the temperature rise is due solely to the transformation of work into energy of molecular agitation. This transformation is rapid, as can be seen by the curves in Figure 7. It is, then, possible to interpret Equation (8), which is valid only for times of extension longer than ten minutes, as representing crystal-

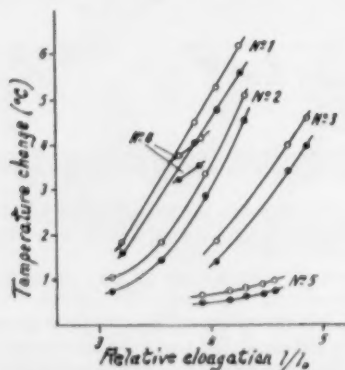


FIG. 8.—Temperature changes of different samples caused by stretching and relaxation, extrapolated to infinite time of elongation, as a function of the percentage elongation, $1/l_0$. In order not to complicate the graph, only the values for a room temperature of 19.5-20.0° C are recorded for sample no. 1.

○ stretching

● relaxation

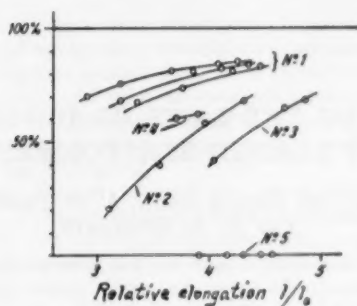


Fig. 9.—The part, in percentage, of the heat effect due to crystallization as a function of the elongation, l/l_0 , of different samples of rubber.

lization as a function of the time in the elongated state. This rate of crystallization corresponds to a first-order reaction, the rate constant K of which varies little with the type of vulcanizate or with the percentage elongation, but rather is a constant characteristic of natural rubber.

SUMMARY

Samples of natural rubber and synthetic rubber were stretched, and the temperature rises were followed by a thermocouple. The heat evolution was found to correspond to an adiabatic process.

The study of the dependence of the heat effect (the Gough-Joule effect) on time shows that, while stretched, rubber crystallizes slowly and the phenomenon can be followed experimentally for several hours.

The final stage of crystallization is probably a first-order reaction, the velocity constant of which is nearly independent of the percentage elongation and which has a small temperature coefficient. On the contrary, fusion following release of the applied stress is relatively rapid.

ACKNOWLEDGMENT

The authors extend their thanks to the French Rubber Institute for placing at their disposal several samples of vulcanized rubber of known compositions.

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A STUDY OF THE LAWS OF DEFORMATION OF LOADED ELASTOMERS *

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Most studies of the laws of deformation of rubbers have been concerned with unloaded vulcanizates. The data of these works are in a number of cases of great scientific interest; but they have no direct practical application, since the great mass of industrial rubber products contain so-called active fillers, usually high-dispersion carbon blacks. Most of the studies of the properties of loaded rubbers were designed to explain the mechanism of reinforcement, that is, to determine why the addition of fillers changes essentially all the physical-mechanical characteristics of rubber. Relatively few investigations have been devoted to a detailed study of the peculiarities of the mechanical behavior of loaded rubber. The work of Patrikeev¹, who studied systematically the phenomenon of "mechanical memory" in loaded vulcanizates of natural and synthetic rubbers, is worthy of mention; for this work was the first to reveal a number of noteworthy effects. Similar studies were made later by Mullins² on loaded vulcanizates of natural rubber. The influence of the content and type of filler and amplitude of deformation on the dynamic properties of loaded rubbers were studied in a number of works of other authors, e.g., Mullins and Fletcher³.

The present study is devoted to a further explanation of the laws of deformation of loaded rubbers. Vulcanizates of sodium-butadiene (SKB) and butadiene-styrene (SKS-30) rubber with various carbon black loadings were the objects of study. In other respects the recipe of the mixtures is standard. The specimens were tested on a float dynamometer⁴, and a Polanyi rigid dynamometer. The specimens were thermostatically controlled during the tests.

The differing mechanical behavior of loaded and unloaded rubbers is evident from observations of stress relaxation at a given deformation. For unloaded rubbers, an elastic equilibrium is achieved within a few hours after stretching, i.e., two stress readings made after a given conventionally chosen interval are equal. In all actual processes, absolute equilibrium is not established, and a state quite near equilibrium is accepted as the equilibrium state. The choice of interval between the two readings in a given case determines the degree of approximation of the equilibrium state. Studies by Bartenev⁵ have shown that, with unloaded rubbers, the observed equilibrium is close to the true equilibrium; this can be demonstrated by either varying the temperature (after a few heating-cooling cycles, the stress values are reproducible at a given temperature) or varying the deformation. Elongation-compression cycles in the deformation range near the original deformation do not change the stress value at this deformation.

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Kolloidnyi Zhurnal*, Vol. 16, No. 3 pages 211-219 (1954).

Similar experiments made with specimens of unloaded rubbers show the conventional nature of equilibrium established when these specimens are kept for a given time at a given temperature, while the conventional nature of the equilibrium is particularly evident if the specimen is subjected to several elongation-compression cycles. This is illustrated in Figure 1, where the relation of stress to deformation, time, and temperature in a sodium-butadiene rubber loaded with carbon black is shown.

The curve of stretching at constant rate up to 100 per cent is shown in Section I of Figure 1, and the relaxation of stress at constant deformation for 60 minutes in Section II. At the end of this period the stress changes very slowly, but further heating (Section III) shows that equilibrium is not yet established. After a few heating-cooling cycles, an apparent equilibrium is reached; its conventional nature is shown by subjecting the specimen to further stretching and compression to 100 per cent. The corresponding value of the stress here is

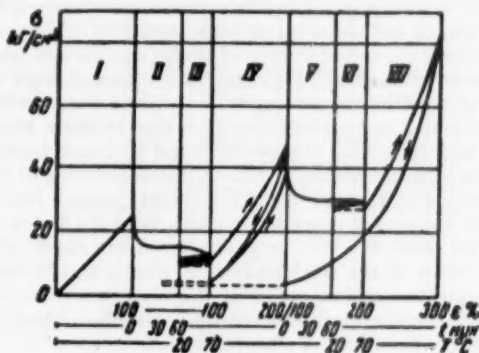


FIG. 1.—Conditional character of elastic equilibrium of loaded rubbers (SKB + 40 parts by weight of channel carbon black).

The ordinate indicates the stress in kg. per sq. cm. The top scale of the abscissa indicates the percentage elongation, the middle scale the time in minutes, and the bottom scale the temperature.

lower than that obtained by heating the specimen at 100 per cent. (see Section IV of Figure 1.) The same relations at 200 per cent are depicted on the other parts of the graph; during compression up to 100 per cent of a specimen stretched to 300 per cent the stress is lower than during compression of a specimen previously stretched to 200 per cent. A similar decrease of stress during compression is observed for unloaded rubbers, and is due to the presence of elastic hysteresis in them.

The essential difference between unloaded and loaded rubbers in this regard is this: while for the former the stress after compression increases gradually to its initial value during this deformation, for the latter this increase is slower, and the stress value established is much lower than the initial value.

Thus the stress established in loaded rubbers as a result of relaxation at constant deformation depends chiefly on the value of the preliminary deformation, i.e., it is non-equilibrant. It should be remarked that the conventionality of the elastic equilibrium established as a result of stress relaxation at room temperature or higher can also be shown by keeping the specimen longer at a given temperature.

At true equilibrium the values of the parameters which describe the state of the system do not depend on the states in which the given system was kept earlier. The rate of approach to equilibrium, determined by the rate of the kinetic process in the system, depends on its structure and on external parameters, such as temperature, stress, etc., and in some cases it may be so small that the state of the system does not change greatly during long intervals. Such states can be formally regarded as states of equilibrium if the parameters of the previous history of the system are included in the external parameters which govern true equilibrium. Examples of such states are the structure of cold metals below the recrystallization temperature, the amorphous state of natural rubber rapidly cooled to vitrification temperature, etc. In both examples, the lower temperatures greatly retard the kinetic processes in these systems and fix their non-equilibrium state. Other parameters which characterize these stable non-equilibrium states are the degree of cold treatment in the first case, and the initial temperature and rate of cooling in the second.

From this viewpoint, it is easy to understand the differences in the mechanical behavior of loaded and unloaded rubbers considered in the preceding section. In unloaded rubbers the establishment of elastic equilibrium (stress relaxation, creep, and elastic after-effect; the latter are regarded here as the gradual establishment of equilibrium deformation of the specimen with increase and decrease of deforming force, respectively) is due to three kinetic processes⁴: rotation of the molecular links around the simple hydrogen bond, redistribution of stresses in the separate molecular chains, and regrouping of the sulfur bonds of the vulcanizate with rupture of the individual chains. During an observation period, only the second process is evident, since the first is completed very quickly, and the third develops very slowly. Thus stress relaxation in unloaded rubbers leads to the establishment of elastic equilibrium after several hours⁵. Consequently, several cycles of stretching and compression near the deformation at which the equilibrium stress is established lead to reproducible stress values at this deformation after relaxation.

In loaded rubbers a fourth process, due to the change in the reaction of the rubber with the particles of filler and the filler particles with each other, is added to the three indicated kinetic processes which govern the rate of establishment of elastic equilibrium, as shown by Dogadkin and Pechkovskaya⁶. This process also proceeds very slowly in the case of active fillers, that is, the completion of the second relaxation process in this case, too, leads to the establishment of apparent elastic equilibrium. A characteristic of this change of the reaction between rubber and filler is a sensitivity to changes of deformation. This is understandable if we assume that the rate of the process depends principally on the stresses in the material, increasing rapidly with an increase of the latter.

The stresses during the established apparent equilibrium will henceforth be called "quasi-equilibrium", and the corresponding values of the modulus, the "quasi-equilibrium modulus", E_{quasi} , regarding both as functions of the previous deformation.

Earlier experiments to determine the influence of previous deformations on the quasi-equilibrium modulus, made on specimens containing various amounts of fillers, have shown that only the maximal deformation has any essential influence on it. Successive deformations cause only a slight change of E_{quasi} . Therefore, in successive experiments, preliminary conditioning of the specimens consisted in stretching them once and keeping them 30 seconds in the stretched state. The tests were made after 15 hours' rest. The residual deformations

obtained from preliminary stretching were not measured, and the deformation during testing was calculated from the length of the specimen before conditioning.

If only the maximal deformation of the specimen has a critical influence on E_{∞} , the value of E_{∞} will not depend on previous deformations less than that which governs the quasi-equilibrium modulus, since the latter is maximal in the given case. The relations of the quasi-equilibrium modulus to the preliminary deformation for vulcanized sodium-butadiene rubber containing various proportions of channel carbon black, shown in Figure 2, fully confirm this fact. Preliminary deformations below $\epsilon = 100$ per cent (at which E_{∞} is determined) do not influence the value of the quasi-equilibrium modulus, and only greater preliminary deformations cause it to decrease.

It is interesting that the relations of the preliminary deformation for rubbers containing various loadings of filler are analogous, but the corresponding relations of the difference $E_{\infty} - E_{\infty}$, where E_{∞} is the equilibrium modulus of

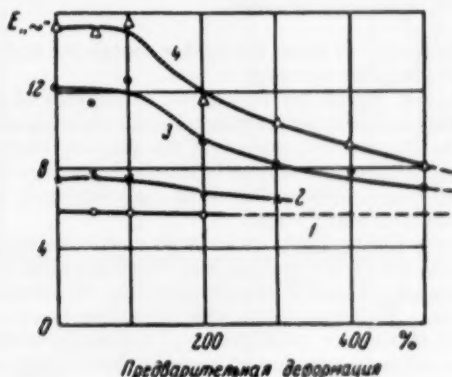


Fig. 2.—Relation of quasi-equilibrium modulus (measured at 100 per cent) to the preliminary deformation of vulcanizates of SBR rubber containing various loadings of channel carbon black. Curve 1.—0, Curve 2.—10, Curve 3.—20, Curve 4.—40 parts by weight.

The abscissa indicates the percentage deformation.

unloaded rubber, are similar. The relation of the relative values of this difference for the three loaded vulcanizates of sodium-butadiene rubber depicted in Figure 2, is shown in Figure 3. As is seen from this diagram, the analogy is reproduced with considerable accuracy. The indicated law was also observed with loaded vulcanizates of other rubbers, as well as in dynamic tests. In this case the difference $E_{dyn} - E_{\infty}$ was considered instead of $E_{\infty} - E_{\infty}$.

Fletcher and Gent⁷ observed a decrease of the dynamic modulus of loaded natural rubber during regular shearing deformations at low amplitude (up to 3 per cent), and found that the decrease of the dynamic modulus with an increase of amplitude of deformation is analogous for rubber containing various amounts of filler and different types of fillers, as long as the specimens are completely vulcanized. In the case of incompletely vulcanized specimens, a more rapid decrease of the dynamic modulus with the amplitude was observed than was to be expected. From our viewpoint, the observed deviations are due only to the fact that a lower E_{∞} value characterizes incompletely vulcanized rubber, and one would expect the relations of the difference $E_{dyn} - E_{\infty}$ to the amplitude of



Fig. 3.—Relative decrease of quasi-equilibrium modulus with increase of preliminary deformation for SKB rubber containing channel carbon black. Point 1 = 10, Point 2 = 20, Point 3 = 40 parts by weight.

The ordinate indicates $(E_{\infty} - E_{\infty})_{rel}$.
The abscissa indicates the percentage deformation.

deformation to be similar to those for rubber containing various amounts of filler with normal vulcanization times.

This interpretation shows the very great importance of the equilibrium modulus of unloaded rubber in defining the behavior of the corresponding loaded vulcanizates. The asymptotic tendency of the quasi-equilibrium modulus toward E_{∞} as the preliminary deformation is increased (see Figure 2) gives reason to believe that the true equilibrium value of the modulus of loaded rubber is equal to E_{∞} , or, at least, nearly equal.

In order to verify this assumption, we performed experiments to determine E_{∞} of specimens after long periods at a given deformation (25–35 hours) at 80° C (the data shown in Figure 2 were obtained after 60 minutes' relaxation at room temperature). The experiments were performed in air and in nitrogen. The experimental results for vulcanizates of sodium-butadiene rubber and butadiene-styrene rubber containing 40 parts by eight of channel carbon black



Fig. 4.—Relation of quasi-equilibrium modulus to the degree of preliminary deformation. Curve 1. SKS-30 rubber + 40 parts by weight of channel carbon black. Curve 2. SKS-30 rubber unloaded. Curve 3. SKB rubber + 40 parts by weight of channel carbon black.

The ordinate indicates E_{∞} in kg. per sq. cm.; the abscissa indicates the percentage deformation ξ .

in 100 parts of rubber are shown in Figure 5. The values of E_{∞} obtained are lower than those presented in Figure 2 (this indicates the conventional nature of equilibrium), but remain as before higher than the corresponding values of E_{∞} designated by broken lines in Figure 4. Thus, both an increase of preliminary deformation and an increase of the relaxation period (and increase of the temperature of relaxation) lead to a decrease of the difference $E_{\infty} - E_{\infty}$, although the latter never becomes zero. It is interesting that the difference, $E_{\infty} - E_{\infty}$, for loaded vulcanizates of butadiene-styrene rubber is less than for vulcanizates of sodium-butadiene rubber, and decreases more rapidly with an increase of the preliminary deformation. This evidently means a weaker reaction between rubber and filler in this case.

By varying the temperature at a given quasi-equilibrium modulus, it is possible to determine the relation of the modulus to the temperature. As is

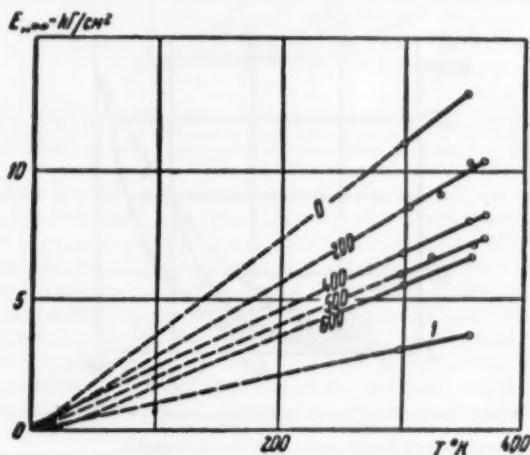


Fig. 5.—Temperature relation of the quasi-crystalline modulus of vulcanizates of SKB rubber containing 40 parts by weight of channel carbon black. The figures on the curves denote the percentage preliminary deformation. Curve 1 is the unloaded vulcanizate.

The ordinate indicates E_{∞} in kg. per sq. cm.; the abscissa indicates the temperature (Absolute).

seen from Figure 5, in which the data for a loaded vulcanizate of SKL rubber subjected to various preliminary conditioning operations are shown, the temperature relations are easily extrapolated to absolute zero temperature. This means that the elasticity of loaded as well as unloaded rubber is governed by the elasticity of the molecular chains; however, the hardness of the latter is increased at the expense of the reaction between the rubber and filler and the hardness of the thixotropic properties of the carbon black structure.

The above mentioned peculiarities of the mechanical behavior of loaded rubbers indicate that this material is very sensitive to preliminary treatment. This is most evident on the stretching curves of specimens subjected to various preliminary conditioning operations. Such series of curves for stretching at constant rate for loaded SKB rubber and SKS-30 rubber are shown in Figure 6. The maximal deformations during preliminary conditioning are indicated by the figures.

It is characteristic of these curves that they can all be clearly divided into two parts, comprising the ranges of initial and repeated deformations. If, in the range of repeated deformations, the course of the curve is such that the greater the preliminary deformation of the specimen, the lower the stresses corresponding to a given deformation in the range of initial deformations, that is, at deformations exceeding the maximal deformation during condition, then the course of the curves does not depend on preliminary deformation.

As has already been mentioned, this phenomenon was first studied by Patrikeev¹ and then by Mullins². The data presented above fully confirm the results of these authors, and give reason to regard the established law as general.

Since the shape of the stretching curve in the range of initial deformations does not depend on preliminary conditioning, we can regard this as an indication of the independence of the properties of the stretched specimen in the range of the preliminary deformations indicated. An interesting illustration of this

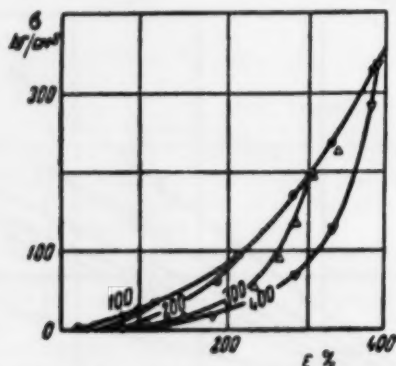


Fig. 6.—Curves of elongation of preconditioned test-specimens: SKB rubber + 40 parts by weight of channel carbon black.

The figures on the curves denote the percentage preliminary elongation.

The ordinate indicates the stress σ in kg. per sq. cm.; the abscissa indicates the percentage elongation ϵ .

is the fact, already observed by several investigators, that the tensile strength of loaded rubber is not affected by preliminary deformations if their number is not too great.

In studying the influence of preliminary deformation on tensile strength, we set up experiments on repeated stretching after rupture, using as specimens strips cut out of the specimen originally ruptured. The data for SKB rubber containing various loadings of channel carbon black are shown in Figure 7. The behavior of a previously ruptured specimen during repeated stretching is interesting because the stretching curves in the range of small deformations practically coincide with the stretching curve of an unloaded vulcanizate, sharply diverge from it at elongations near the deformation at rupture, and intersect the curve of the first elongation near the rupture point.

A study of the effect of preliminary conditioning on the mechanical properties of loaded rubbers would be incomplete without considering the recovery of their original mechanical properties with time. Observations showed that this restoration takes place very slowly. Figure 8 shows the curves of repeated stretching of a number of specimens of loaded sodium-butadiene rubber (40

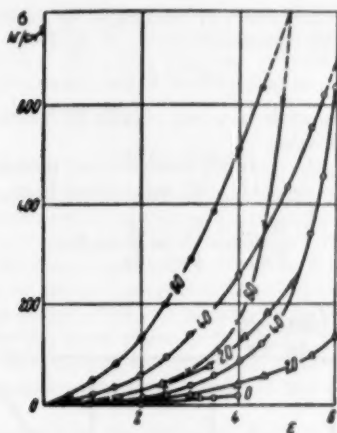


Fig. 7.—Influence of preliminary deformation on the tensile strength of vulcanizates of SKB rubber. The figures on the curves denote the channel carbon black content in parts per 100 parts by weight of rubber. The ordinate indicates the stress σ in kg. per sq. cm.; the abscissa indicates the percentage elongation ϵ .

parts by weight of channel carbon black) rested for various periods between the first and second deformations. The figures on the curves denote the period of rest in days; the upper curve represents the first stretching. The first stretching of all the specimens was carried to the point of rupture. It is seen from Figure 9 that even a long rest, for example, 5.5 months, at room temperature by no means restores the original properties of the material (less than 50 per cent).

The importance of E_x for characterizing the mechanical properties of loaded rubbers is particularly evident in the description of their dynamic properties. The fundamental characteristics of the material during dynamic tests are the dynamic modulus E_{dyn} and losses per cycle in a unit volume. The latter

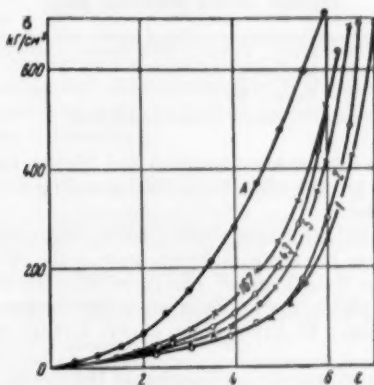


Fig. 8.—Influence of rest on the shape of the curves of stretching under constant stress; SKB rubber + 40 parts of channel carbon black.

The figures on the curves denote the rest period in days. Curve A indicates the initial elongation. The ordinate indicates the stress σ in kg. per sq. cm.; the abscissa indicates the percentage elongation ϵ .

will be called "friction modulus", k , relating it by analogy with the dynamic modulus by means of the equation⁸:

$$\Delta W = k \cdot \epsilon^2_0$$

where ΔW is the loss per cycle in a unit volume of deformed material, and ϵ_0 is the amplitude of deformation.

For loaded rubbers, the dynamic modulus and modulus of friction increase with an increase of filler content. We established that

$$\frac{E_{dyn} - E_{\infty}}{E_{0dyn} - E_{\infty}} = \frac{k}{k_0} = f(c) \quad (2)$$

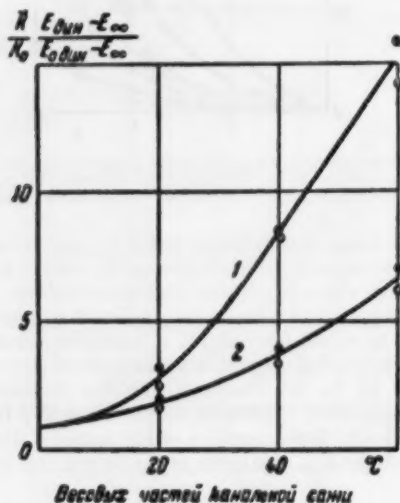


FIG. 9.—Relation of the relative values of modulus of friction and non-equilibrium part of the dynamic modulus to filler content. Curve 1.—SKB rubber. Curve 2.—SKS-30 rubber.

The ordinate indicates the $\frac{k}{k_0} = \frac{E_{dyn} - E_{\infty}}{E_{0dyn} - E_{\infty}}$ values.

The abscissa indicates the parts by weight of channel carbon black.

where E_{dyn} and k are the dynamic modulus and friction modulus for a loaded rubber, E_{0dyn} and k_0 are the same for a corresponding unloaded vulcanizate; and c is the filler content.

If we assume that E_{∞} is the true equilibrium modulus of loaded rubber, then this relation shows that the nonequilibrium part of the dynamic modulus and the friction modulus of loaded rubber, compared with the corresponding values for unloaded rubber within the limits of error, are expressed as a function of the filler content alone. In the present study, further confirmation of this law was obtained.

The method⁹ of spontaneous contraction of the rubber strips was used to determine E_{dyn} and k . The results of these measurements¹⁰ for vulcanized sodium-butadiene rubber and butadiene-styrene rubber containing various loadings of channel carbon black are presented in Figure 9.

A study of previously conditioned specimens showed that preliminary deformations, although changing the value of $f(c)$ for a given filler content, do not invalidate Equation (2). Thus, this equation is valid also for loaded rubbers subjected to preliminary stretching, if f is regarded as a function of loading and maximal preliminary deformation.

CONCLUSIONS

1. Prolonged storage of loaded specimens at a given deformation (stretching) causes the establishment of an apparent equilibrium, which, it is assumed, is characterized by the "quasi-equilibrium modulus", E_{∞} .

2. The value of the quasi-equilibrium modulus E_{∞} depends on the preliminary deformation to which the specimen is subjected, while the maximal deformation has the greatest effect. A number of repeated constant deformations gives practically the same effect as the first. With an increase of the maximal preliminary deformation, the quasi-equilibrium modulus tends asymptotically toward the equilibrium modulus E_{∞} of the corresponding unloaded vulcanizate.

3. Proportional changes in the difference $E_{\infty} - E_{\infty}$ with respect to the preliminary deformation does not depend on the filler content. A similar law is observed with respect to the dynamic modulus E_{dyn} .

4. The relation of $\frac{E_{dyn} - E_{\infty}}{E_{dyn} - E_{\infty}}$ to the filler content and preliminary conditioning coincides, within the limits of experimental error, with the analogous relation for the relative values of the friction modulus of the rubber.

5. The laws enumerated indicate that the cause of the observed changes of elastic properties with loading is the sharp increase of the unequilibrium part of the stress in the material. The great sensitivity of this part of the stress to deformations and slow recovery during rest suggest an analogy between loaded rubbers and thixotropic colloid systems in a low-molecular dispersion medium.

6. The linear temperature relation of the quasi-equilibrium modulus is extrapolated to absolute zero. This indicates the entropic nature of elasticity of loaded rubbers.

7. The influence of preliminary deformations on the mechanical properties of loaded rubbers is most evident on the curves of stretching at constant rate. It can be seen that the properties of the material in the range of deformations greater than the preliminary deformation do not depend on this previous deformation. The tensile strength of loaded rubbers does not depend on the extent of preliminary deformation.

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6. Dogadkin, Pechkovskaya and Dashevskii, *Kolloid. Zhur.* 10, 357 (1948); Pechkovskaya, Mil'man and Dogadkin, *Kolloid. Zhur.* 250 (1952); Dogadkin, Pechkovskaya and Mil'man, *Kolloid. Zhur.* 14, 346 (1952).
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8. The dynamic modulus is related to the total energy applied per cycle in a unit volume of deformed material, according to the relation:

$$W = \frac{E_{dyn} \cdot \epsilon^2}{2}$$

⁹ Reznikovskii and Khromov, *Kolloid. Zhur.* 14, 3, 77 (1952).

¹⁰ These measurements were made by M. K. Khromov, to whom the authors express their sincere gratitude.

EXPERIMENTAL DETERMINATION OF THE DYNAMIC VISCOSITY AND ELASTICITY AND ALSO THE RELAXATION TIME SPECTRUM OF RUBBER.

III.*

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INTRODUCTION

In Parts I and II of our recently published papers¹ it was shown that the relaxation time spectrum of rubber can be obtained by measuring the flow curve, i.e., change in length as a function of time with constant load. In addition, it was shown that knowledge of the relaxation time spectrum makes possible the prediction of the dynamic viscosity and the dynamic elasticity of the test sample. This paper reports experiments which prove and, as would be anticipated, confirm these theoretically found relationships².

For all cases in the range in which the time dependence of the degree of elongation $\alpha = L/L_0$ of a test material deformed with a constant load σ can be represented by the equation:

$$\frac{\alpha - 1}{\delta} = \frac{1}{E'} = \frac{a + \ln t}{b} \quad (1)$$

the relaxation time spectrum according to Parts I and II, i.e., the density $dE_0/d\tau$ of the partial elastic moduli in the various ranges of the relaxation time τ , is given by the relation³:

$$\frac{dE_0}{d\tau} = \frac{b}{\tau} \cdot \frac{1}{[\ln(c\tau - 1)]^2 + \pi^2} \quad (2)$$

where

$$\ln c = a - 0.577 \quad (2a)$$

Conversely, as Parts I and II have shown¹, the visco-elastic behavior which is to be expected for any stress applied to the sample is established completely by this relaxation time spectrum. Thus, the strains in a sample periodically deformed with an angular velocity ω can be described by a dynamic elastic modulus $E(\omega)$ and the heat developed by a dynamic viscosity $\eta(\omega)$:

$$E(\omega) = \frac{b}{\ln c - \ln \omega} \quad (3)$$

$$\eta(\omega) = \frac{b \cdot T}{4 \times 2(1 + \mu)} \cdot \frac{1}{[\ln(c/\omega - 1)]^2 + \pi^2} \quad (4)$$

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As an approximation for the dependence of the viscosity on the period $T = 2\pi/\omega$ the following relationship results⁴:

$$\eta(T) = \frac{b}{a^2} \cdot \frac{T}{12} \quad (5)$$

Experimental proof of this relationship which is characteristic for the relaxation time spectrum decides the question of whether or not the distribution expressed in Equation (2) is actually realized in a given material.

The following points are of special importance.

1. The viscosity observed in the case of a torsional vibration, occurring with a period T , depends mainly on the portion of the spectrum in which the relaxation times are slightly shorter than the period T . As has been shown⁴, the greatest part of the heat of friction developed by the swing is, indeed, caused by the restoring-force mechanisms, whose relaxation time τ is somewhat shorter than T .

From the viscosity increment ($\Delta\eta$) which results by increasing the period to ΔT , can thus be determined directly the intensity of those regions of the relaxation time spectrum whose relaxation times τ lie between T and $T + \Delta T$. The fact that the quotient $\Delta\eta/\Delta T$ is, according to Equation 5 a constant, is almost completely guaranteed if the relaxation time spectrum in the limited region in which τ is nearly equal to the period can be represented by Equation (2). It was, therefore, of interest to prove experimentally the proportionality⁴ of $\eta(T)$ with the period T required by Equation (5).

2. In order to compare the absolute values of the viscosity $\eta(\omega)$, calculated by Equations (3) and (4), and the elastic modulus $E(\omega)$ with experimental values, knowledge of the constants a (or $\ln c = a - 0.577$) and b is necessary. These constants must be determined according to Equation (1) from the creep curve (time function of deformation α at constant load σ).

3. During the course of the investigation, an observation was made which had not been anticipated, and which made an extension of the experimental problem necessary: The dynamic viscosity $\eta(T)$ for a period T and a given temperature was found to depend on the state of stress of the test sample. Therefore, viscosity had to be examined for rubber samples which were given a constant elongation, on which the periodic stress used for the viscosity measurement was superposed.

MEASURING THE DYNAMIC VISCOSITY AND THE DYNAMIC ELASTIC MODULUS OF RUBBER

DESCRIPTION OF THE APPARATUS

The apparatus used to measure the dynamic viscosity is sketched in Figure 1. A gyrating mass (3) is fastened to a thin steel wire (1) (diameter 0.1 or 0.2 mm., length 170 mm.). The moment of inertia I can, by addition of iron disks, be varied between 100 and 6,000 grams per sq. cm. The rubber sample to be examined (about 5 cm. long and of 5-10 sq. mm. rectangular cross-section) is secured at (4) to the gyrating mass. Its lower end is held at (6) in such a way that no torsional movement, but only a vertical displacement, of this point is possible. By the weight (7) and the counter weight (8), the rubber sample can be subjected to an arbitrary, but constant, vertical pull. To carry out the measurements, an angular momentum around the vertical axis is imparted to

the gyrating mass (3), so that it sets up a damped torsional vibration. The amplitude of this swing and its period can be measured by a beam of light which is reflected on a mirror (2) and falls on a scale located 1 meter away.

CALCULATION OF THE DYNAMIC VISCOSITY AND DYNAMIC MODULUS OF ELASTICITY FROM THE EXPERIMENTAL DATA

Let the clamped rubber sample of length L , width A , and thickness B have a dynamic viscosity $\eta(\omega)$ (defined on the basis of the heat developed per unit volume for a given rate of deformation) and a dynamic elastic modulus $E(\omega)$.

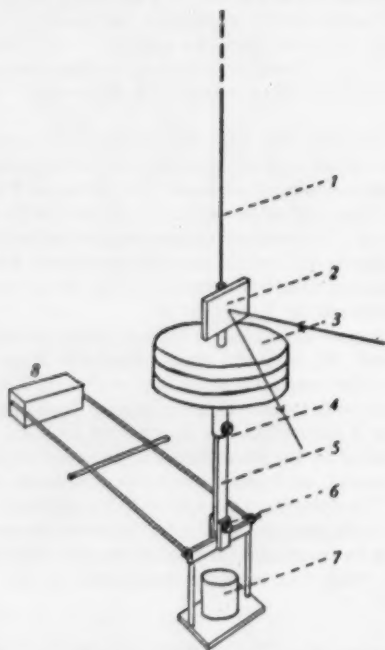


Fig. 1.—Apparatus for measuring the vibration viscosity and the dynamic modulus of elasticity of rubber.

The system (1, 3, 5 in Figure 1) swinging freely then experiences a damped harmonic vibration. The angle γ through which the system is rotated from its resting position at the time t will be given by the relation:

$$\gamma = \gamma_0 \cos \omega t \cdot e^{-kt} \quad (6)$$

where

$$\omega^2 = \omega_0^2 + E(\omega) \frac{I_p}{I \cdot L(2 + 2\mu)} - k^2 \quad (7)$$

and

$$k = k_0 + \eta(\omega) \cdot \frac{I_p}{2I \cdot L} \quad (8)$$

where

$$I_p = \frac{1}{12} (A^3 B + A B^3) \quad (9)$$

is the polar surface moment of inertia of the cross-sectional area $A \times B$ of the rubber sample, I the axial moment of inertia of the entire vibrating system. The frequency and the damping constant of the swing observed when the rubber sample 5 in Figure 1 is omitted from the system are expressed as ω_0 and k_0 .

$$\gamma = \gamma_0 \cos \omega_0 t \cdot e^{-k_0 t} \quad (10)$$

μ is Poisson's number (= 0.50 for rubber). From Equations 7 and 8 we obtain:

$$\eta(\omega) = (k - k_0) \cdot 2 \frac{I \cdot L}{I_p} \quad (11)$$

$$E(\omega) = (\omega^2 \cdot \omega_0^2 + k^2) \frac{I \cdot L(2 + 2\mu)}{I_p} \quad (12)$$

To determine k and ω , the maximum deflections on both sides were measured, as well as the time. There results from Equation (6) for the amplitude γ_n remaining after expiration of n periods:

$$\gamma_n = \gamma_0 \cdot \cos 2n\pi \cdot e^{-k(2n\pi/\omega)} = \gamma_0 \cdot e^{-k(2n\pi/\omega)} \quad (13)$$

or

$$\ln \gamma_n = \ln \gamma_0 - \frac{2n\pi \cdot k}{\omega} \quad (14)$$

The amplitude, expressed by Equation (13), is not identical with the maximum deflection, the so-called pseudo-amplitude, because of damping. The two parameters differ only in a constant factor which does not influence any of the conclusions which follow. Equation (14) is thus also valid for pseudo-amplitude². If in γ_n , the logarithm of the n 'th amplitude value, is plotted against n , the number of periods, a straight line is obtained, from whose slope k can be determined.

Tests were made on unstretched samples and on samples stretched in the direction of the torsion axis to the α -fold of the original length. When the values relating to the unstretched state are given an index 0:

$$I_p = I_{p0} \cdot \frac{1}{\alpha^3} \quad (15)$$

$$L = L_0 \cdot \alpha \quad (16)$$

and, consequently,

$$\eta(\omega) = (k - k_0) \cdot \frac{2I \cdot L_0}{I_{p0}} \cdot \alpha^3 \quad (11a)$$

$$E(\omega) = (\omega^2 - \omega_0^2 + k^2) \frac{I \cdot L_0(2 + 2\omega)}{I_{p0}} \cdot \alpha^3 \quad (12a)$$

GENERAL EXPERIMENTAL CONDITIONS

The experiments were performed with three different sheets taken from the same piece of vulcanized rubber⁷. This vulcanized rubber consisted of 95 per cent high-grade Para rubber, with zinc oxide, age resistor, accelerator, and sul-

fur. It was vulcanized 25 minutes at 127° C. All the experiments were carried out in a constant temperature room at $20.0 \pm 0.1^\circ \text{C}$.

The dimensions of the apparatus (Figure 1) were so chosen that damping would be rather small. In each experiment, about 10–20 swings could be observed, so many points were available to determine the damping constant k according to Equation (14). The amplitude of the swing observed decreased from about 10° to 0.50 , i.e., by about a factor 20. If smaller amplitudes were employed, disturbances caused by air currents became noticeable. The shear deformation produced in the rubber sample itself was, of course, much smaller; the angle of shear was about 0.5° maximum in the vicinity of the surface of the test sample.

RESULTS OF VIBRATION EXPERIMENTS

Independence of the viscosity with respect to the amplitude.—According to van der Wyk⁷, the viscosity should increase rapidly with increase of amplitude. In this case the k values in Equation (6) would have to depend on the amplitude,

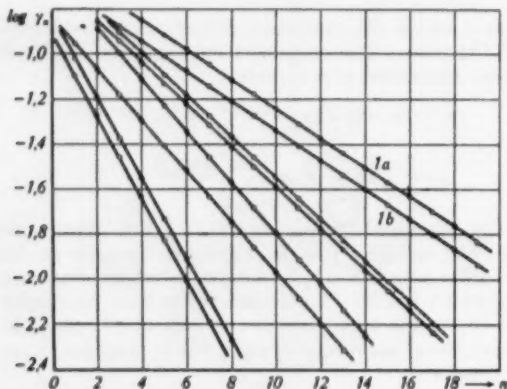


FIG. 2.—Damping of torsional vibration.

The logarithm of the amplitude of the angle of torsion, $\log \gamma_n$, is plotted against n , the number of periods. The calculations are based on Equation (14). Each pair of curves, e.g., curves 1a and 1b, represent two experiments using different initial amplitudes γ_0 , but otherwise the same experimental conditions.

and they ought, therefore, to change in the course of an experiment, i.e., greater at the beginning than toward the end. The curve of $\ln \gamma_n$ plotted against n (Equation 14) would, then, be steeper at the beginning than at the end.

In all of our experiments, however, a systematic deviation from the straight line was never found. Aside from occasional disturbances by air currents, the points lie almost on a straight line (Figure 2). The scattering of the $\ln \gamma_n$ values around the straight line is about 0.003 to 0.01 for the individual experiments. This corresponds to an average deviation of γ_n values of 0.4–1 per cent.

In our case, the vibration viscosity in the region of 1 to 30 angular minutes is thus independent of the angle of shear.

In the course of the experiment, the internal temperature of the rubber is bound to increase, since heat is developed by friction in the sample. The total amount of thermal energy produced in this way amounted to a temperature increase of only about 10^{-5}°C .

The logarithm of the amplitude of the angle of torsion, $\log \gamma_n$, is plotted against n , the number of periods. The calculations were made from Equation (14). The two curves, e.g., curves 1a and 1b, correspond to two experiments using different initial amplitudes γ_0 , but otherwise with the same experimental conditions. The average ordinate deviation of the points from the curve is 0.025–0.1 mm. (shown in Figure 2), the maximum deviation 0.1–0.4 mm.

Reproducibility.—The k values from various experiments, which were made consecutively without changing the experimental conditions, correspond very well. The average difference between such consecutive k values is about 1 per cent. The absolute reproducibility is less perfect. First of all, determining the effective length of the rubber sample and its state of stress involves an uncertainty; second, after stronger deformation, relaxation and crystallization processes take place, which can still exert a certain influence on viscosity hours

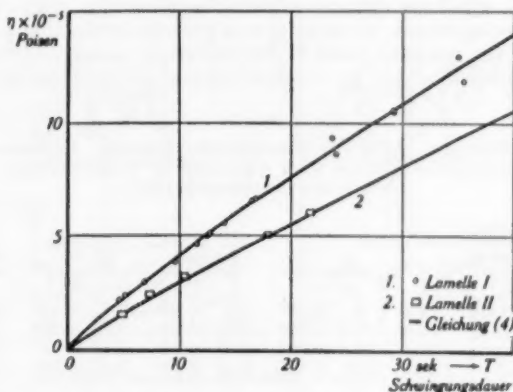


Fig. 3.—The viscosity η of rubber determined from damping measurements is approximately proportional to the period T . The experimental data are for Samples I and II. The values obtained with Sample I are shown as circles on curve 1; those obtained with Sample II as rectangles on curve 2. The curves are drawn from values calculated theoretically from Equation (4).

For curve 1, $a = 14.2$; $b = 10.5 \times 10^7$ dynes per sq. cm.

For curve 2, $a = 18.5$; $b = 12.6 \times 10^7$ dynes per sq. cm.

The abscissa indicates the vibration period in seconds. The ordinate indicates the viscosity η in poises.

later. The uncertainty amounts to about 5 per cent in the absolute numerical values of viscosity in the case of unstressed rubber and about 10 per cent in the case of stressed rubber.

Viscosity as a function of time.—As was pointed out under point 1 of the introduction, emphasis was placed on proving the proportionality of $\eta(T)$ with the period T required by Equations (4) and (5).

Figure 3 shows the results of experiments on unstressed rubber. In these experiments, the period T was varied between 5 and 35 seconds by changing the gyrating mass. The η values obtained for two different sheets which, however, were cut from the same slab, are plotted against T . Each point, corresponding to an average of two to three individual experiments, was calculated from the slope of two or three damping curves, like those given in Figure 2. To compare the experimental values with those expected theoretically, two curves, calculated according to Equation (4), were constructed in Figure 3.

For curve 1, $a = 14.2$, $b = 10.5 \times 10^7$ dynes per sq. cm.; for curve 2, $a = 18.5$, $b = 12.6 \times 10^7$ dynes per sq. cm. The a values, as a comparison with those below in Table 3 shows, are equal to the experimentally found values for the same sheet from the elongation creep curve (change of length with constant load). However, numbers were used for the b values which are approximately 15 per cent greater than the values calculated from the elongation creep curve. This point will be discussed later.

Figure 3 shows that the experimentally determined points fall along the calculated curve within the limit of error. Consequently, the dependence of the dynamic viscosity μ on the period T can actually be represented by Equations (4) or (5). The approximate proportionality of μ with the period T predicted is confirmed.

The absolute value for the proportionality factor in Equations (4) and (5) is obtained almost, though not quite, exactly by substituting the numerical values a and b , which are determined from the elongation creep curve (Equation 1), in these equations, which refer to a periodic torsional stress of rubber. The fact that the absolute value of the vibration viscosity $\eta(T)$, e.g., for a period $T = 20$ seconds, with an absolute value $\eta = 7 \times 10$ poises, can be cal-

TABLE 1
THE CONSTANTS a AND b FOR UNSTRETCHED RUBBER. COMPARISON OF
CALCULATED VALUES WITH VISCOSITY ($T = 20$ SECONDS)
MEASURED EXPERIMENTALLY

Sample	Type of creep curve for measuring the constants, a and b	a	b (dynes per sq. cm.)	η/T (poises per sec.) Equation (4)	η/T (poises per sec.) Equation (5)	η/T (poises per sec.) Data from the damping of torsional vibration
I	Stretching	14.2	9×10^7	3.4×10^4	3.7×10^4	3.9×10^4
II	Stretching	18.5	11.1×10^7	2.53×10^4	2.70×10^4	2.75×10^4
III	Stretching	20.5	12.5×10^7	2.33×10^4	2.47×10^4	2.55×10^4
III	Torsion	13.2	5.3×10^7	2.23×10^4	2.55×10^4	2.55×10^4

culated from the elongation creep curve with an accuracy of 15 per cent may serve as proof of the fundamental correctness of the ideas advanced in the first two papers of this series². The 15 per cent deviation between the calculated and the experimental absolute values of η may, as will be shown below, be partially due to the fact that the density $dE_0/d\tau$ of the partial elastic moduli in the relaxation time spectrum for very small values is somewhat larger than is given by Equation (2). This has already been indicated in Part II.

On the other hand, it should be remembered that the stress necessary for measuring the constants a and b from the elongation creep curve and the torsion necessary for measuring the dynamic viscosity by periodic torsional stress cause anisotropy in the sample. The anisotropy is not the same for the elongation creep curve as for the torsional vibration. The constants a and b were determined from the elongation creep curve and also from a torsional flow curve, and, as was anticipated, distinctly different values were found for a and b for the same sample. (See Table 1, especially the second last and last columns.) This will be discussed later.

The anisotropy caused by a stress in the test samples will presently be discussed.

Viscosity as a function of the degree of elongation.—To see how the arrangement of the network filaments in rubber is influenced by stretch and how this arrangement affects the viscosity, consider Figure 4. It illustrates schemati-

cally the influence of stretching the sample in the x -direction on the frictional resistance toward a shear deformation superimposed on the stretch. Owing to a preferred orientation of the individual network filaments in the x -direction, the sliding movement of the x - y planes is facilitated in the x -direction, and the viscosity decreases.

In periodic torsion of a sample stretched in the x -direction around the x -direction as an axis, shear movement does not result parallel to the original direction of elongation, but 45° to it. But this is insignificant for qualitative considerations.

If the test sample is, after sudden stretching, kept at constant length, the parallel arrangement of the network filaments will be partially lost as a result of relaxation. This means that the viscosity of the stretched sample will be particularly small when it is measured immediately after stretching and that it later increases if the sample is maintained at constant length.

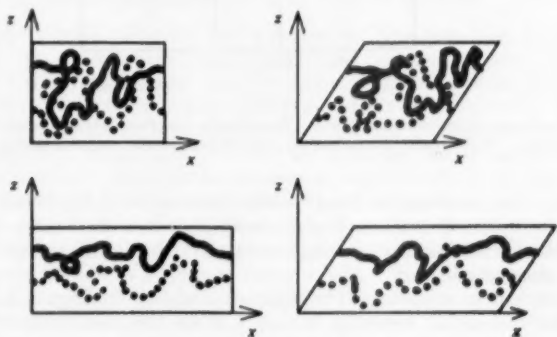


FIG. 4.—Model concept showing the dependence of viscosity on the degree of elongation.

Upper models: not stretched. The interlaced molecular chains cannot slide over one another during shear deformation.

Lower models: stretched. The chain segments in parallel alignment can slide over one another.

Both phenomena, the decrease of viscosity when the sample is stretched and the time dependence of the extent of decrease, were observed in the experiments.

In Figures 5a and 5b, the values of η/T (which practically no longer depend on T) are plotted against the degree of elongation α . The viscosity is seen to decrease sharply, even with small degrees of elongation. For greater degrees of elongation, it probably reaches a constant value which is about half as large as the viscosity of the unstretched sample. An accurate determination of the initial values (viscosity of the unstretched sample) is not possible, since disturbances are caused by even the smallest stresses, e.g., the weight of the sample itself.

The increase of viscosity with time for a sample which is kept at a constant degree of elongation, i.e., the influence of a decrease of the perfectness of the parallel arrangement of the network filaments can be seen from Figure 5a. In order to obtain the experimental points shown in this figure, the degree of elongation of the rubber (see Figure 1) was from one point of the curve to the next each time increased by increasing the weight (7 in Figure 1), a viscosity measurement being taken 10 minutes after producing the particular degree of

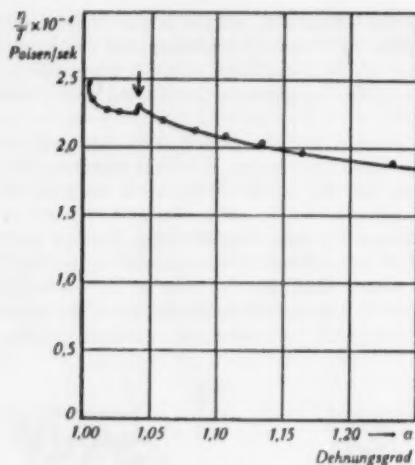


Fig. 5a.—Viscosity as a function of elongation α . Experiments using Sample III. Period T approximately 20 seconds. At the arrow—Increase of viscosity through partial relaxation during 1 hour.

elongation. An exception in this procedure was made at the point, marked by an arrow in Figure 5a, where the viscosity was measured after keeping the degree of elongation constant during one hour. During this time, the viscosity increased about 2 per cent.

Dynamic elastic modulus.—The apparatus shown in Figure 1, which was designed for measuring viscosity, does not allow the measurement of the dy-

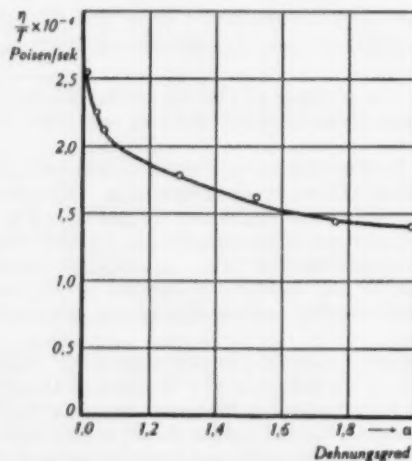


Fig. 5b.—Viscosity as a function of elongation α for a larger range of α . Experiments using Sample III. $T = 20$ seconds.

dynamic elastic modulus with too great accuracy. Since $E(\omega)$ depends little on ω , its exact determination is not of great interest in this work.

The following values are for a period of 20 seconds:

Sample I $E_{dyn} = 4.8 \times 10^6$ dynes per sq. cm.

Sample II $E_{dyn} = 4.1 \times 10^6$ dynes per sq. cm.

Sample III $E_{dyn} = 3.3 \times 10^6$ dynes per sq. cm.

In contrast to the viscosity, the dynamic elastic modulus is practically independent of the degree of elongation. Of course for greater degrees of elongation it must be taken into consideration that the force, necessary for vertical elongation during the torsion of the test-specimen, also contains horizontal components which produce an additional moment of rotation around the vertical axis. This portion was eliminated in the calculations of E_{dyn} (See Equation 19a below).

MEASUREMENT OF THE CREEP CURVE

It has already been indicated that a relaxation time spectrum according to Equation (2) and the relationships (3), (4), and (5) resulting therefrom must be realizable if the creep curve of the substance examined is given by Equation (1). Whether, and how accurately, this occurs for a given material has to be determined by experiment; in a similar way also, the numerical values of the constants a and b in Equation (1), which are necessary for an accurate test of Equations (4) and (5), must be determined experimentally from case to case.

As indicated above, it is necessary to make some reservations in calculating the effects occurring with periodic torsional stress from the elongation creep curve, because the anisotropic effects produced in the test sample do not exactly correspond for the two types of experiments. It has been deemed necessary to investigate the analogous torsional creep process in addition to the elongation creep process which is the basis of Equation (1). As already indicated, the constants a and b are not identical for the elongation and the torsional creep process.

DESCRIPTION OF THE APPARATUS

Elongation creep curve.—To determine the elongation creep curve, the clamped rubber test-specimen was stretched with a constant force by suspending a weight. The progress of the elongation was measured visually, using a telescope with a thread micrometer.

Torsional creep process.—For a quantitative determination of the torsional creep process, a modification of the apparatus in Figure 1 was used. While the lower portion of the apparatus (parts 2, 3, 4, and 5) was held in the rest position, the upper end of the steel wire 1 (about 0.1 mm.) was rotated through a definite angle (e.g., through 5 entire revolutions) from its rest position. In place of the gyrating mass 3 in Figure 1, an arresting device was used, which could be released electrically. To prevent vibration, the moment of inertia of the part of the apparatus set into motion by releasing the arrestor was made as small as possible. After releasing the arrestor, the rubber sample 5 was subjected to a torsional stress which was practically constant. From this time on, the angle through which the upper end 4 of the rubber sample had moved from the rest position was measured as a function of the time t . By choosing a suitable weight 7 (Figure 1), the sample 5 to be examined for torsional creep could be stretched by an arbitrary factor α in the longitudinal direction before applying torsional stress.

For measuring the angle of torque, the setup in Figure 6 was used. Light from a slit 4 was reflected from the semi-transparent mirror 5 upon mirror 3 attached to the upper end of the rubber sample. From here the light fell on a mirror 2, which could be rotated around the axis of 3. Mirror 2 was secured to a graduated dial 1. The mirror was rotated so that the light beam was reflected in itself. Through the semi-transparent mirror 5, the light fell on hairline 7 of the ocular of the telescope 6. Figure 6 shows that the slit of light 4 was always focused on the hairline 7 when the graduated dial, with its attached mirror 2, was rotated exactly twice the angle through which mirror 3 was turned. This angle can be read on the graduated dial to 1/100 degree accuracy, using a microscope and interpolating with a linear micrometer. At times during the experiments, mirror 2 was somewhat advanced. Since mirror 3 rotated slowly, the image of the slit traveled through the visual field of the telescope 6. The

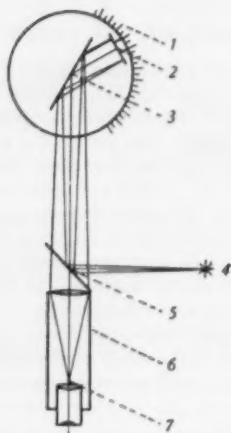


FIG. 6.—Optical arrangement for measuring small rotations in determining the torsion creep curve.

time at which it coincided with the stationary hairline 7 could be determined accurately to 1/2 second.

For the apparatus described, parallel displacements of mirror 3 in the designated plane, which are difficult to prevent for this loose suspension, play hardly any role.

CALCULATION OF THE CREEP CURVES

From elongation measurements.—By definition, the creep curve shows the change of length with the load constant. In these elongation experiments, as also in Brenschede's experiments⁵, a constant force was used. Stress (= force: actual cross-sectional area) increases during the course of an experiment corresponding to a reduction of the cross-sectional area. Since the change is small, it is only taken into consideration by introducing the actual stress in the calculation of $1/E'$, thus:

$$\frac{1}{E'} = \frac{\Delta L}{L_0} \cdot \frac{1}{\sigma} = \frac{1}{\sigma_0} \cdot \frac{1 - \alpha}{\alpha} \quad (17)$$

The definition (17) of E deviates from one frequently used in which the stress is based on the original cross-sectional area, i.e., where:

$$\frac{1}{E} = \frac{\Delta L}{L_0} \cdot \frac{1}{\sigma_0} = \frac{1}{\sigma_0} \cdot (1 - \alpha)$$

If the actual stress were to change greatly during an experiment, the entire computation of the relaxation time spectrum, in which the assumption of constant stress is important, would have to be modified.

The values of $1/E'$ plotted against $\ln t$, give the creep curve.

From torsion experiments.—For calculating the torsion experiments, the following expression is used:

$$\frac{1}{E'} = \frac{1}{3G} = \frac{I_p \cdot \gamma}{3M \cdot L} = \frac{I_{ps} \cdot \gamma}{3M \cdot L_0 \cdot \alpha^2} \quad (18)$$

where γ is the angle of torque, M the moment of rotation acting upon the rubber, L_0 the length, and I_{ps} the moment of inertia of the surface of the cross-sectional area of the unstretched rubber sample. $\alpha = L/L_0$ signifies the relative increase in length of the rubber sample in the direction of the axis produced by the weight γ , and G is the modulus of torque.

Thought must also be given to the fact that the moment of rotation M is not entirely constant. On the one hand M depends little on γ , on the other hand, for stretched as well as for torsion-stressed rubber, a component of the vertical force due to the weight γ acts in the direction of M and increases the modulus of torque. This has nothing to do with the relaxation phenomena being investigated and must, therefore, be eliminated. For the resulting moment in Equation (18), we thus have:

$$M = (\beta - \gamma) \cdot f - \gamma \cdot f' \quad (19)$$

$$f' = \frac{I_{ps} \cdot K}{L_0 \cdot F_0 \cdot \alpha^2} \quad (19a)$$

where β is the angle through which the steel wire is rotated before the experiment, f its constant torsion (moment of rotation: angle of rotation), K the force necessary for stretching the sample 5 by a factor α and F_0 the original cross-sectional area of the rubber sample.

RESULTS

Several torsional creep curves, which were obtained at different degrees of elongation, are reproduced in Figure 7 and correspond to the elongation creep curves in Figure 8. The points in Figure 7 (torsion measurements) lie almost exactly in a straight line. The average deviation of the points from the individual straight lines is 0.1–0.3 per cent of the average value for $1/E'$ for moderate degrees of stretch (α to about 1.4).

The dependence of the relaxation phenomena on the degree of elongation appears from the noncoincidence of the curves which correspond to different loads. The moment of torque was equally large in all cases.

The curves for the elongation measurements (Figure 8) deviate appreciably from a straight line. This is partially caused by the following.

Measurements were taken one after the other with the same sample, whereby the sheet was unloaded for only about 1 hour between the individual

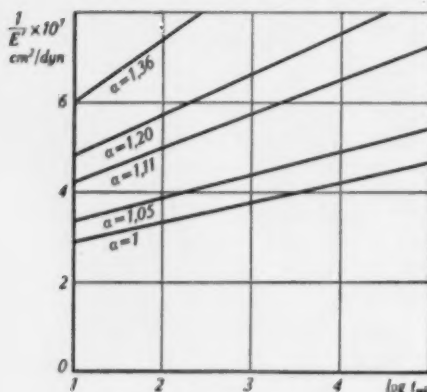


FIG. 7.—Torsion creep curves.

Dependence of the creep curves on a preliminary deformation of the test sample in the direction of the torsion axis through a factor α . Experiments with Sample III. $1/E'$ is graphed as the ordinate, i.e., the reciprocal of the E modulus resulting from the angle of torque observed at time t (Equation 18). The abscissa is the logarithm of time t (measured in seconds).

experiments (for the torsion measurements about 12 hours). Obviously in this time the modifications which are associated with large relaxation times have not completely retrogressed. With renewed load, some of these mechanisms may act in the direction of the applied stress up to a certain deformation and only then, i.e., at still higher deformation in the opposite direction, thus first they may accelerate stretch and then retard it. The first part of the curve will then be steeper than for completely "rested" rubber, the second part as steep or flatter. This effect can be clearly seen in curve 3, which was taken

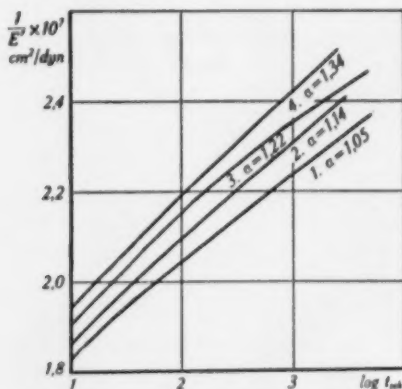


FIG. 8.—Elongation creep curves.

Experiments with Sample III. $1/E'$ is the ordinate, i.e., the reciprocal of the E modulus resulting from the change of length ΔL observed at time t (Equation 17). The abscissa is the logarithm of the time t (measured in seconds). In curve 1 the constant load is small, so small that the value observed after 10^4 seconds was equal to $\alpha = L/L_0 = 1.05$. For the other curves, the loads were larger, the α values observed for $t = 10^4$ seconds being equal to 1.14 (curve 2), 1.22 (curve 3), and 1.34 (curve 4).

after only 25 minutes' rest period. Thus, the curvature is, at least partially, a result of the rubber sample used.

However, it is apparent that the entire curvature cannot be explained in this way. Actually there exists a certain deviation in the course of the relaxation time spectrum from the curve given by Equation (2), E' increasing more rapidly when passing into the region of smaller times t than according to Equation (2).

Figures 7 and 8 once again indicate clearly that, for lightly vulcanized rubber, data on the elastic modulus are of very limited value if they are not supplemented by data concerning the time (after stretching) at which the restoring force or the dilation was measured. If, for example, in the case of our test-piece, the change of length is measured 1 minute after the beginning of the deformation, an elastic modulus is obtained which is about 15 per cent larger than if it is measured after 1 hour.

In Table 1, columns 3 and 4, are given several values for a and b obtained from the elongation and torsion creep curves. From these values, the viscosity and the value of η/T were calculated according to Equation (4) and according to the approximation (5) (see columns 5 and 6). They may be compared with the experimental values determined from the damping of torsional vibration (see column 7).

The table shows: (1) the values of a and b , which are obtained from the elongation creep curve and the torsion creep curve, deviate considerably from one another (see the last two horizontal lines in Table 1). As already mentioned, the mechanical changes produced in the network filaments partly oriented in the mechanically stretched rubber sample differ greatly for the two methods of measurement. Obviously, as a result of this, partly different types of relaxation mechanisms enter in the function if the two types of measurement are carried out.

A comparison of the a and b values determined from the elongation creep curves for the three samples (line 1, 2, and 3 of Table 1) shows considerable differences, although the three samples were taken from the same rubber sheet, obtained at different distances from the surface of the sheet, parallel to the surface. Since Sample III came from the surface of the rubber sheet and Samples I and II from the interior, it is possible that the state of vulcanization of these sheets varied somewhat. Aging may also have exerted a greater influence on the surface than on the interior.

In spite of the difference of the a and b values, the viscosity computed therefrom corresponds in each case within the limit of error (± 5 per cent) with that found experimentally. The fact that the values computed from the approximate Equation (5) agree better with the experimental values is regarded as chance compensation of various deviations. It should, rather, be concluded that the values calculated according to the exact formula generally are somewhat too low. This permits certain conclusions for the course of the relaxation time spectrum in the region of very small relaxation times.

In Table 2 the experimentally determined dynamic elastic modulus is compared with that calculated according to Equation (3). The values, computed from the torsion measurements, agree to some extent with the experimental ones (last line). The values calculated from the elongation creep curves, deviating sharply from the E values reported from the torsion measurements, show again that it is impossible to convert the constants resulting in different types of deformation into one another exactly applying the hitherto used

formulas. A more complete description of the viscoelastic behavior could be done in tensorial form.

The dependence of the values of a , b , η_{dyn} , and E_{dyn} on the degree of elongation is given in Table 3. Of prime importance was the question as to whether the strong dependence of viscosity on the degree of elongation can be explained by a change of the a and b values. For small degrees of elongation, a decrease

TABLE 2
DYNAMIC MODULUS OF ELASTICITY. COMPARISON OF CALCULATED
VALUES WITH MEASURED VALUES ($T = 20$ SECONDS)

Sample	Type of creep curve for measuring constants a and b	E_{dyn} (dynes per sq. cm.) Calculated from Equation (3)	E_{dyn} (dynes per sq. cm.) Experimental data from torsional vibration
I	Stretching	6.1×10^6	4.8×10^6
II	Stretching	6.0×10^6	4.1×10^6
III	Stretching	6.1×10^6	3.3×10^6
III	Torsion	$3.9\text{--}3.2 \times 10^6$	3.3×10^6

of the viscosity actually results from these values, according to Table 3. The amount of the decrease corresponds approximately with the experimental findings (see column 4 and 5). For greater elongations, the range of error becomes too large as the result of introducing significant correction terms for calculating a and b (Equations 19 and 19a).

The dynamic elastic modulus depends very little or not at all on the degree of elongation.

TABLE 3
DEPENDENCE OF THE VISCOSITY AND MODULUS OF ELASTICITY ON THE
DEGREE OF ELONGATION. SAMPLE III ($T = 20$ SECONDS)

Degree of elongation	a	b (dynes per sq. cm.)	η/T (poises per sec.) Equation (5)	η/T (poises per sec.) Experimental	E_{dyn} (dynes per sq. cm.) Equation (3)	E_{dyn} (dynes per sq. cm.) Experimental
1.00	13.2	5.32×10^7	2.55×10^4	2.55×10^4	3.90×10^6	3.26×10^6
1.02	13.0	4.55×10^7	2.25×10^4	2.35×10^4	3.36×10^6	3.30×10^6
1.05	13.1	4.38×10^7	2.12×10^4	2.20×10^4	3.20×10^6	3.28×10^6
1.11	10.8	3.11×10^7	2.22×10^4	2.00×10^4	2.73×10^6	3.24×10^6
1.20	10.1	2.56×10^7	2.12×10^4	1.85×10^4	—	—
1.35	9.5	2.50×10^7	2.30×10^4	1.75×10^4	—	—
2.00	—	—	—	1.40×10^4	—	—

FURTHER DISCUSSION OF THE RESULTS

ACCURACY OF THE MEASUREMENTS

Accuracy of the measurements. The greatest difficulty encountered in the measurements is establishing the momentary internal state of the sample and reproducing it in different experiments. Apart from the irreversible changes, such as aging, tearing of the network links, etc. (which did not enter into the phenomenon noticeably), reversible processes occur, whose course is to be considered as uncontrolled as far as those reversible processes are concerned, are slow in comparison with the time available for the experiments and the time between the experiments. In addition to crystallization and dissolution of the

crystals, mechanical relaxation processes in the broadest sense belong to this group of reversible processes. Improving the methods of measurement does not eliminate these difficulties; on the contrary, it can make them more prominent.

The range of error might be narrowed by more accurate a definition and standardization of the history of the piece of rubber under investigation. Greater certainty of the values obtained would also be possible by increasing the number of experiments, using exactly the same conditions and evaluating them statistically.

CONCLUSIONS CONCERNING THE RELAXATION TIME SPECTRUM BASED ON THE η VALUES

In spite of these limitations, certain general conclusions can be drawn from a comparison of experimental and theoretical values.

1. The proportionality of the viscosity and the period (Figure 3 and Equation (5)) found in agreement with theory, supports the assumption of a continuous and monotonous density $dE_0/d\tau$ of the relaxation time spectrum, the density increasing approximately proportional to $1/\tau$. There is, in a large range of τ values, not the slightest indication of the existence of discrete relaxation times nor of local agglomerations or maxima in the continuous spectrum. This is certainly true for relaxation times between about 10^{-1} and 10^4 seconds, and it is hardly to be assumed that beyond this region the spectrum suddenly becomes essentially different.

The actual viscosities are somewhat larger than those resulting from the relaxation time spectrum. This can be interpreted by the portion of the spectrum with short relaxation times contributing more strongly than corresponding to the (extrapolated) Equation (2). This would also explain the faster fall of the creep curve with shorter times, and thus the convex curvature (Figure 8). The same conclusion has already been reached¹ on the basis of a summation rule concerning the integral of the E_0 values.

PRACTICAL IMPORTANCE

In view of the great differences in the viscosities found even for similar samples of rubber, it hardly pays, in general practice, to measure viscosity with very great accuracy, since the values measured for one piece of a large sample cannot even be applied to the entire sample (see Table I, last column). On the other hand, for many applications it is extremely important to know the approximate viscosity for a periodic deformation at a definite frequency, since the internal heat development depends on this. A direct measurement of viscosity, e.g., with the apparatus of Figure 1, involves some expenditure. On the other hand, measurement of the creep curves by measuring elongation as a function of time is exceptionally simple. For an orientation on the position and steepness of the creep curve, it is sufficient to make one measurement of the length of the deformed sample, e.g., in the time interval between 10 seconds and 15 minutes after application of the load. The viscosity for any frequency can then be calculated directly from the creep curve, using Equation (5).

SUMMARY

For the purpose of testing recently published theoretical relationships, the dynamic viscosity and dynamic modulus of elasticity of a lightly vulcanized

rubber were measured. In these experiments, a sample of rubber in sheet form was inserted axially in a torsion pendulum system, so that the sheet was subjected to a periodic torsional deformation. Because of the dynamic modulus of elasticity of rubber, the frequency, and because of the dynamic viscosity, the damping of the resulting swing, are modified.

In the region examined, the viscosity, η , is independent of the amplitude of the periodic deformation. The viscosity, η , does, however, depend on the period T of the swing to which the sample is subjected, i.e., η is practically proportional to the period T . Thus, (η/T) is approximately constant. With the samples used in the experiments, the magnitude of the ratio, η/T , was found to be approximately $(2.5-4) \times 10^4$ poises per second.

If the rubber is stretched along the torsion axis, the viscosity decreases, and for an elongation of 100 per cent, η is about one-half as great as for the unstretched rubber. The reduction of viscosity is greater immediately after stretching than at some later time after stretching. The reduction of viscosity and its time dependence can be plausibly related to a model.

The dynamic modulus of elasticity is almost independent of the period that the sample is deformed torsionally, as well as of the elongation along the torsion axis. For the samples tested, $E_{\text{dyn}} = (3-5) \times 10^6$ dynes per sq. cm.

In order to obtain a more accurate test of the theoretical relationships, the creep curve was measured in addition to the dynamic viscosity and E modulus of one individual sample. Measurements of the linear creep curve were made, i.e., the time dependence of linear deformation at constant load, as well as of the torsional creep curve, i.e., the time dependence of the torsion angle at constant torque.

The deformation, represented as a function of the logarithm of time, is a straight line in the torsion experiment and almost a straight line in the linear elongation experiment. In both these experiments, the location and slope of the flow curves defines the constants a and b , from which the absolute value of the viscosity η , e.g., for a period of 20 seconds, could be calculated. This calculated value of η agrees well with the experimental values; small deviations indicate that the density distribution of the relaxation times is increasing somewhat more than in proportion to $1/\tau$ in the region of very small relaxation times.

The constants a and b derived from the linear creep curves and from the torsion creep curves differ considerably, although the η values, computed from their combination, are almost the same. This may be due to the fact that the rubber becomes anisotropic when it is deformed and that this anisotropy affects the restoring forces and the relaxation phenomena differently in the case of linear deformation and in the case of torsional deformation.

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TESTING OF RUBBER FOR ITS LOW-TEMPERATURE STABILITY BY MEASUREMENT OF THE LOSS OF ELASTICITY *

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AND R. S. KONENKOV

By the low-temperature stability of rubber we understand the retention of its high elastic properties when cooled below 0° C. The problem of low-temperature stability of vulcanized rubber arises from the fact that its high elastic properties are evident only within a limited temperature range because of the relaxation characteristics. This temperature range depends, not only on the nature of the rubber, but also on the conditions of deformation, especially on the time t of application of the force.

The low-temperature stability of a test sample will serve to characterize that of the corresponding rubber product itself only when the following factors are taken into account in testing the sample:

(1) The specific physical properties of the rubber, which have a decisive importance in the performance of the particular product, and in relation to which the method of testing for low-temperature stability must be chosen;

(2) The extent to which the index of low-temperature stability depends on the experimental conditions, i.e., on the dimensions of the test-specimen, the nature of the stresses, etc. Here any test must take into account the service conditions, which have a strong influence on the index of low-temperature stability. The low-temperature stability of rubber can be determined by changes in the following physical properties caused by lowering of the temperature: (1) deformability; (2) recovery; (3) brittleness; (4) temperature contraction; and (5) crystallizability². There is no question that the most fundamental of these properties is the loss of high elasticity, as indicated by the increase of hardness. In this case the coefficient of low-temperature stability is derived from the relation:

$$K = \frac{\epsilon}{\epsilon_{20}}$$

where ϵ is the deformation at the given temperature and ϵ_{20} is the deformation at room temperature for the particular system. It is assumed that, at 20° C, a rubber product is in the high elastic state under practically all service conditions.

Considering the above-mentioned deficiencies of certain specifications and testing apparatus, the authors developed a method of testing vulcanized rubber for low-temperature stability by its loss of elasticity during any time of deformation. The temperature T_K , at which the hardness of the rubber increases $1/K$ times, was taken as the index of low-temperature stability.

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INFLUENCE OF CONDITIONS OF DEFORMATION ON THE COEFFICIENT OF LOW-TEMPERATURE STABILITY

As has already been observed, the temperature range of transformation from the high elastic to the vitreous state, and, consequently, the temperature T_K , depends on the deformation system.

Alexandrov and Lazurkin³ showed that this range is displaced by a change of frequency of the stress during periodic loading or by a change of the time of application of the stress under a uniform static load.

Experiments made by the authors have shown that the low-temperature stability of soft rubber does not depend on the dimensions of the specimen, or on the deformation (up to 30 per cent compression or 300 per cent elongation), or on the type of deformation (elongation, compression, or bending). Figure 1

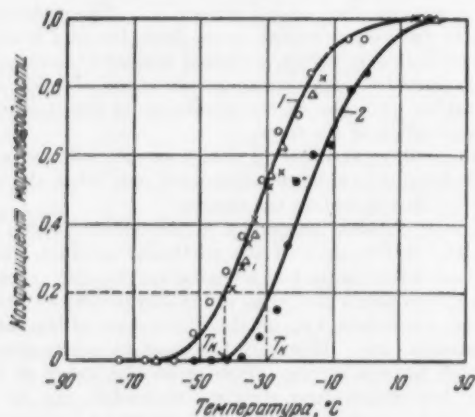


Fig. 1.—Relation of coefficient of low-temperature stability to temperature for an unloaded vulcanizate of butadiene-acrylonitrile rubber SKN-18 (○ 15% compression; × 15% elongation; △ 250% elongation; ● 15% amplitude of compression).

1. Static deformation $t = 30$ seconds
2. Dynamic deformation $\nu = 1500$ oscillations per minute

The ordinate indicates the coefficient of low-temperature stability. The abscissa indicates the temperature (Centigrade).

gives data for compression and elongation. Since bending is a combination of compression and elongation, the results can be generalized for the case of bending. The difference indicated in the amount of deformation is slight; it is seen in Figure 1 that these variations have no significance.

The equivalence of static and dynamic systems established by Lazurkin⁴ was confirmed. The indexes of low-temperature stability T_K coincide, with periodic loading, frequency ν , and a static load with the indicated time t of stress (see Figures 2 and 3) when the following relation is maintained:

$$t = \frac{1}{2\nu} \quad (1)$$

The results make it possible: (1) to determine the index T_K , which characterizes the low-temperature stability of the rubber as a material, using specimens

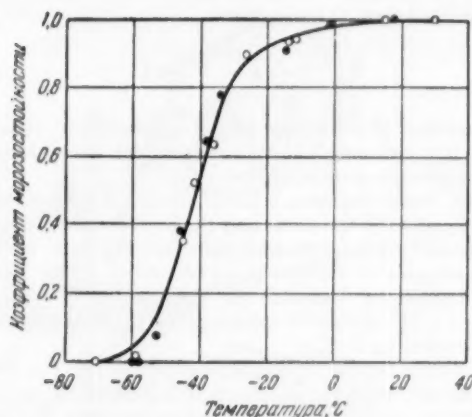


Fig. 2.—Relation between coefficient of low-temperature stability and temperature for an unloaded vulcanizate of butadiene-styrene rubber SKS-30 (● 1 oscillation per minute; ○ 30 seconds). Data obtained with an oscillographic relaxometer¹.

The ordinate indicates the coefficient of low-temperature stability. The abscissa indicates the temperature (Centigrade).

of any uniform shape and size; (2) to apply the results of the test to any values of compression, elongation, or bending of the rubber product during service; and (3) to apply the index of low-temperature stability of both static and dynamic loads to service conditions.

It is important only to consider the influence of the period of application of the deforming stress on the low-temperature stability of rubber. This time is regarded as the entire period of application of the stress for a static load, and half-period of vibration for an alternating load (as is seen from Equation 1). The index of low-temperature stability T_K can be obtained from the curve which gives the relation of the coefficient low-temperature stability to the temperature (see Figure 1). The relation between T_K and the period of application

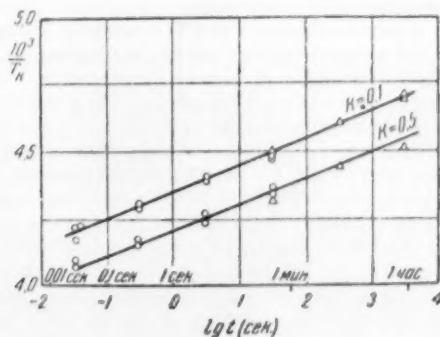


Fig. 3.—Relation between index of low-temperature stability and period of application of force (Δ static deformation; ○ dynamic deformation). Data obtained with an oscillographic relaxometer¹.

The abscissa indicates $\lg t$ (seconds).

of the stress is derived from the equation:

$$\frac{1}{T_K} = A_K - B \cdot \log t \quad (2)$$

where A_K is a constant of the rubber at a given coefficient of low-temperature stability K , and B is a constant of the rubber which is independent of the coefficient of low-temperature stability.

This equation, which indicates a linear relation between the logarithm of the period of application of the stress and the inverse index of low-temperature stability, is confirmed by experimental data (see Figure 3) for both unloaded and loaded vulcanizates of various types of rubber. This relation was first experimentally derived by Lazurkin for the case of $K = 0.5$. One of the present authors (G. M. Bartenev) later derived this relation theoretically for any value of K , excluding $K \ll 1$.

The simple relation between the temperature T_K and the deformation system makes it possible, when the constants in Equation (2) are known, to find without difficulty the index of low-temperature stability T_K for the material studied at any period or frequency of the applied force encountered in practice. On this basis, a method of determining the index of low-temperature stability of a rubber is described below, which involves the measurement of $1/T_K$ at any two values of the time t . According to these values, which are depicted graphically as two points, a curve can be drawn with the coordinates $1/T_K = f(\log t)$. The curve completely characterizes the low-temperature stability of a given rubber for a given coefficient of low-temperature stability. Any point on this curve corresponds to the specific characteristic of the rubber for any given time of application of the force.

Since it is necessary to have the greatest distance between the two original points in order to construct the curve accurately, a new apparatus was developed with which it is possible to determine the original curve $K = \varphi(T)$, on the one hand, for a period of several minutes, e.g., 5 minutes, of static deformation and, on the other hand, for a very small period (a fraction of a second) of periodic deformation at a frequency of 1500 cycles per minute (which corresponds to $t = 0.02$ second). It is easy to maintain a constant amplitude of force with this apparatus at any temperature and time by means of an eccentric which is regulated during operation of the apparatus.

The apparatus, shown in Figures 4 and 5, consists of a ring (1), operated, from the motor (2), by an eccentric by means of a coupling (3). Ring (1) has a slot into which a ball-bearing fits, mounted on an eccentric. The slot enables the eccentric bearing to move freely horizontally, while the vertical motion is limited. Thus the eccentric bearing, moving in the slot of the ring, compels the latter to move vertically upward and downward. This also assures a strictly sinusoidal application of the load, not only during compression, but also during recovery of the specimen, which is not provided by other machines. The movement of the ring is transmitted by the post (4). This post is firmly fastened to springs, comprising block (5), which consists of two springs of different stiffnesses, connected in parallel. The large outer spring is connected on the bottom with a post (6) which presses on the test-specimen placed in a socket. This socket can be moved in the direction of the length of the specimen by means of a micrometric screw (7). The deformation of the specimen and the load on it are measured by mirrors (8) and a scale (9) as follows. Light rays from the source (10) are reflected by the mirrors according to the deformation

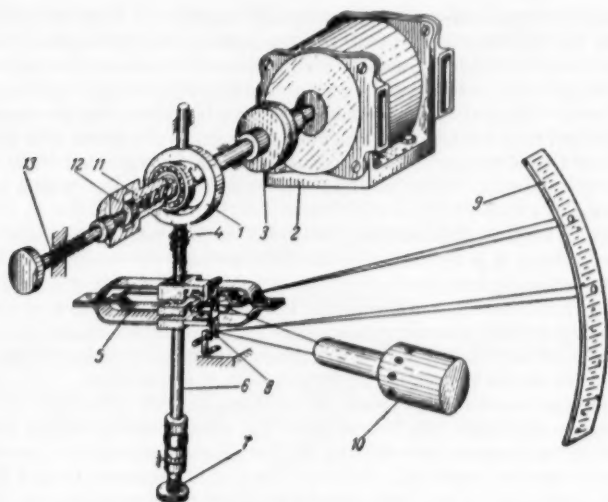


FIG. 4.—Schematic view of the apparatus.

and stress, and give two corresponding reflections on the translucent scale. When the apparatus is operating, the mirrors are rotated by angles proportional, for one mirror, to the deformation of the specimen, and for the other mirror, to that of the stressing spring. The reflections on the scale move correspondingly. The displacement of the reflections is greater, the greater is the scale distance.

The following principles were utilized in order to regulate the operating eccentricity of the apparatus. The eccentric bushing (11) has three threads, with a spacing of about 30 mm. The eccentric sleeve (12), with a screw thread inside corresponding to that of bushing (11), is placed over the latter. The eccentricity of the sleeve is equal to that of the bushing. Changes of the eccentricity are obtained by rotating the eccentric sleeve with respect to the bush-

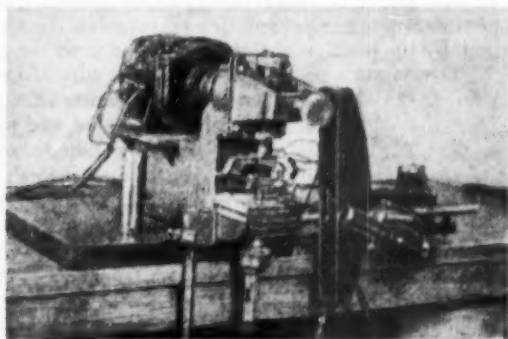


FIG. 5.—Photograph of the apparatus.

ing. Their eccentricities are geometrically additive. The eccentricity is controlled by the displacement of the eccentric sleeve (12) along the axis. When the sleeve is displaced axially with respect to the eccentric bushing, the sleeve, because of its screw thread, rotates, and thereby changes the eccentricity of the system. Axial displacement of the sleeve is effected by the screw (13), which is turned by a handle. The screw is fastened to the sleeve (12) by a ball-bearing and a split retainer. The eccentricity can be regulated while the apparatus is in operation. The maximum eccentricity is 2 mm., which will give a ring travel of 4 mm.

In this method of determining the index of low-temperature stability of vulcanized rubber, it is necessary to take into account the service conditions of a product containing any particular type of rubber. For this it is sufficient to know the low-temperature stability for the period of application of the force corresponding to the operating conditions of the product, since it has been established that the coefficient of low-temperature stability does not depend on the amount or on the conditions of deformation of the rubber.

The test-specimens were prepared in the shape of solid cylinders 8×10 mm.

In order to determine the temperature T_K , which corresponds to the given coefficient of low-temperature stability K , the selection of which is governed by the technical service conditions of the product, it is necessary to find the relation of the coefficient of low-temperature stability (deformation ϵ) to the temperature (see Figure 1) for the two systems. To this end, an arbitrary amount of deformation suitable for the measurements, e.g., 10 per cent, is imposed. The stresses which cause this deformation in both systems, static and dynamic, are determined at room temperature.

For periodic deformations of a given amplitude, the motor is switched on and rotated at 1500 rev. per min. This corresponds to a period of 0.02 second.

To obtain a static deformation of a given magnitude, the motor is switched off, and the load is applied for 5 minutes.

The test-specimen is cooled to -70°C and kept for 10 minutes at this temperature. The lowest temperature at which it is possible to begin measurements is that at which the coefficient of low-temperature stability is less than 0.01, i.e., the sample can be more than 100 times as stiff as at room temperature. Then the temperature of the test-specimen is slowly raised, while the given stress amplitude is maintained by means of the eccentricity regulator, which is adjusted according to the position of the reflection on the scale. Every $3-4^\circ \text{C}$, the amplitude of deformation is measured: (1) under periodic deformation, by the amplitude of vibration of the deformation reflection on the scale; (2) under static deformation, by the position of the same reflection at the end of the deformation period. During this period, the eccentric is adjusted so as to maintain a constant force. In this way, curves are constructed for both systems (see Figure 1), and then the values of T_K are calculated and plotted on the graph (see Figure 3). The linearity can be verified by adding another period of static compression; for example, 30 seconds or 30 minutes. Such a verification must be made, since it is impossible to predict the existence of strict linearity for rubbers of any given composition.

If in technical experiments, there are no definite data available from which to select a definite value of the coefficient of low-temperature stability, then two values of T_K can be chosen, corresponding to the standard values of K (0.1 and 0.5), which include practically all possible actual cases, where the high elasticity of the material is essentially unchanged.

The indexes of low-temperature stability $T_{0.1}$ and $T_{0.5}$, shown in Figure 3, are the desired characteristics of the low-temperature stability of the material.

In conclusion, the difference between the low-temperature stability of a material and the performance of the product in service at low-temperatures should be emphasized. The serviceability of a product depends both on the low-temperature stability of the rubber parts and on the construction of the product, the quality of which can greatly influence performance in service. In any analysis of the latter, it is necessary to consider this important fact, and to bear in mind that the lowest temperature at which a product is serviceable is governed not only by the low-temperature stability of the rubber parts, but also by the good or bad construction of the product.

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THERMODYNAMICS OF CRYSTALLIZATION IN HIGH POLYMERS. NATURAL RUBBER *

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INTRODUCTION

In various crystalline polymers, the degrees of crystallinity range up to 90 per cent and the sizes of the crystallites are such that a given molecule can participate in more than one crystallite. A crystalline polymer that is not subjected to any external stresses can be considered to consist of a collection of connected but randomly oriented crystallites embedded in an amorphous matrix. It might appear that, for systems possessing such a complex morphology, the possibility of any quantitative description of its behavior is precluded. However, it has been demonstrated¹ that, when many crystalline polymers are heated slowly, the temperature at which the last traces of crystallinity disappear is well defined, reproducible, and independent of any previous thermal history of the sample. This temperature is the one of thermodynamic significance, for it is the temperature at which the most perfect crystallites are unstable relative to the pure polymeric liquid, and hence can be identified with the equilibrium melting temperature, T_m^0 of the polymer. Slow heating is of the utmost importance, since conditions are then fulfilled to yield ultimately only the more perfect crystallites; the imperfect crystallites melt at temperatures well below T_m^0 . If the heating is conducted rapidly, as is customary for low molecular-weight materials, then the melting temperature that is observed², depends on the previous thermal history of the sample, and is of uncertain thermodynamic significance. In particular, this melting temperature will depend on the temperature of the crystallization or the manner in which the crystallization was induced. For polyesters³ and polyamides⁴, such behavior has been clearly demonstrated to be a consequence of fast heating; when slow heating rates are employed, an equilibrium melting temperature has been shown to exist.

The establishment of T_m^0 has allowed the application of a thermodynamic analysis to the melting process⁵. Thus, the effect of extraneous ingredients as low molecular-weight diluents on lowering T_m^0 can be predicted and assessed by appropriate experiment. For natural rubber, Wood and Bekkedhal⁶ have shown that the melting temperature on fast heating varies from about 0° to 30°, depending on the crystallization temperature. The seeming lack of an equilibrium melting temperature in this polymer has led to the opinion that its fusion process cannot be described by a thermodynamic analysis.

Since thermodynamic analysis has contributed greatly to an understanding of the crystallization behavior of other polymers, it is important to inquire whether an equilibrium melting temperature does exist for natural rubber. This question can best be answered by experiments in which, for the reasons mentioned above, the melting process must be carried out extremely slowly.

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EXPERIMENTAL

Materials.—Three samples of natural rubber were used in this study. Two of the samples were molecular-weight fractions and were identical to two of those used by Wagner and Flory⁷ in their study of the molecular configuration of natural rubber. The number-average molecular weights of these samples were 119,000 and 280,000, respectively. The third sample, though heterogeneous in regard to molecular weight, had been subject to an extensive purification procedure following the method of McPherson⁸. This purified sample consisted of 98.7 per cent rubber hydrocarbon, 0.44 per cent protein, and 0.18 per cent ash. To this sample 1.00 per cent of phenyl- β -naphthylamine was added as antioxidant.

The diluents, methyl oleate (Eastman Kodak Co.), *n*-dodecane (The Matheson Co.) and *n*-tetradecane (Eastman Kodak Co.), were of technical grade, and were used as received. Their densities were measured at two widely different temperatures, and a linear variation between these temperatures was assumed.

The rubber-diluent mixtures were prepared by dissolving about 3 g. of the polymer together with an appropriate amount of diluent in 30 ml. of benzene. The solution was frozen at the temperature of an ice-water mixture and the benzene removed by subliming for 24 hours. The polymer-diluent mixture was then weighed, and the amount of diluent which remained was computed. The volume fractions of the two components were computed at the melting temperature of the mixture.

The dilatometric methods⁹ previously described in great detail were followed in the present work, the dilatometers being immersed in a constant temperature bath where temperature was regulated to within $\pm 0.1^\circ$ in the range studied.

RESULTS AND DISCUSSION

Pure Natural Rubber.—The dependence of the specific volume on temperature for a molecular-weight fraction of natural rubber for four different crystallization temperatures, T_c , is shown in Figure 1. For clarity in presentation, the curves have been arbitrarily displaced along the ordinate. This plot is typical of the observations for the other two samples of natural rubber studied. The significant thermal history of the samples consisted of the transfer from a temperature above the melting point to the predetermined crystallization temperature. After sufficient crystallinity had developed, the dilatometric observations were made in the order of ascending temperature, employing slow heating rates. Up to 15° , the temperature was increased at the rate of about $1^\circ/12$ –24 hours, and at each temperature the volume first increased for about 6 to 12 hours, then decreased, and reached a constant value within the prescribed time. This behavior is typical of the melting process in polymers¹⁰ and is apparently due to the partial melting of imperfect crystallites and the subsequent formation of more perfectly ordered regions. Above 15° , the heating rate was decreased to about $1^\circ/24$ –48 hours, and a similar behavior was observed in the volume-time relation, though at temperatures within 3 – 5° of the melting temperature, the subsequent decrease of volume was absent. The variations of the specific volume with time at a fixed temperature, as just described, are applicable to the melting process subsequent to crystallization at -18 , 0 and $+8^\circ$. At 14° approximately 100 days were required for the development of sufficient crystallinity to permit satisfactory observations. In this case the variations of the volume with time, at any given temperature on

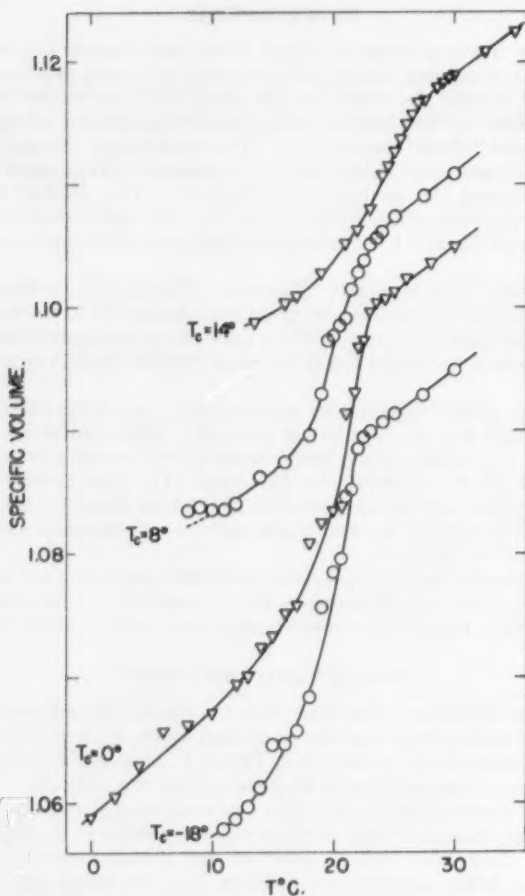


FIG. 1.—Specific volume as a function of temperature for a molecular-weight fraction of natural rubber, $M_n = 119,000$. Each curve represents heating cycle subsequent to crystallization at the indicated temperatures, and all are arbitrarily displaced along ordinate. For actual specific volumes add $0.004 \text{ cm}^3/\text{g.}$ to the -18° crystallization curve; subtract 0.006 from the 0° curve; subtract 0.012 from the $+8^\circ$ curve; subtract 0.020 from the $+14^\circ$ curve.

subsequent heating, were much less than that observed after crystallization at the other temperatures.

The specific volume-temperature plot of Figure 1 indicates quite clearly the temperature at which the last traces of crystallinity disappear, and these values are listed in Table I. The results for the crystallization at -18 , 0 and $+8^\circ$ are, within experimental error, independent of both the crystallization temperature and the individual samples. On fast heating⁶, the variation of the temperature at which melting was complete is about 20° , ranging from $+2^\circ$ for crystallization at -18 to 22° for crystallization at $+8^\circ$. For crystallization at $+14^\circ$, we observe on slow heating a melting temperature 5 – 6° higher than for the

lower crystallization temperatures. This is a reflection of the more perfect degree of order that is achieved by a slow crystallization process, which is also manifested in the small changes observed in the volume-time relations. The melting temperature following 14° crystallization, namely, $28 \pm 1^\circ$, must then be close to the true equilibrium melting temperature.

There are many reports of types of natural rubber whose melting temperatures appear to be much greater than 28° , and this phenomenon also needs explanation in the light of the assignment of 28° as T_m^0 for natural rubber. Rubber which has been stretched beyond its normal limit can be given a large set by cooling. Such rubber is termed "racked rubber", and its x-ray diffraction patterns show that it is composed of highly oriented crystallites¹¹. On subsequent heating the crystallites disappear in the vicinity of 35 to 40° , and the melting process is accompanied by a large retraction¹². Since the crystallites are oriented, the connecting amorphous regions must necessarily be deformed from their statistically more probable configuration (though no external stresses are maintained), and it is then expected that the crystallites will be stable at higher temperatures compared to the undeformed system. Another variety of natural rubber is "stark rubber"⁶, which is normally found crystalline

TABLE I
MELTING TEMPERATURES OF NATURAL RUBBER SAMPLES AFTER
CRYSTALLIZATION AT THE INDICATED TEMPERATURE

Crystn. temp., (T_c) ($^\circ$ C)	M.t. (T_m) ($^\circ$ C)		
	Sample I $\bar{M}_n = 119,000$	Sample II $\bar{M}_n = 200,000$	Sample III Purified rubber
-18	22 -22.5	21 -21.5	21 -22
0	22.5-23	21.5-22	22.5-23.5
+ 8	23.5-24	21.5-22	22.5-23
+14	27 -28	25.5-26	28 -29

at room temperature, and whose melting temperature is in the range 35 to 45° . Recent x-ray diffraction investigations¹³ of several different varieties of stark rubber indicate that its crystallites are also oriented.

When these anomalies are accounted for, natural rubber displays a melting behavior that is typical of polymeric materials. The low melting points can be attributed to the low temperature of crystallization and the subsequent rapid heating rates employed. The abnormally high melting points of racked and stark rubber are due to the internal stresses and orientation of the amorphous regions caused by the orientation of the crystallites.

Polymer-Diluent Mixtures.—The addition of a lower molecular-weight diluent to a semicrystalline polymer lowers the equilibrium melting temperature in a manner similar to the depression of the melting temperature of a low molecular-weight crystal. By the application of the thermodynamic principles governing the melting in binary systems it has been shown that¹⁴:

$$1/T_m - 1/T_m^0 = (R/\Delta H_u)(V_u/V_1)(v_1 - \chi_1 v_1^2) \quad (1)$$

where T_m is the melting temperature of the polymer-diluent mixture, R is the gas constant, ΔH_u the heat of fusion per mole of repeating unit, V_u the molar volume of the repeating unit, V_1 the molar volume of the diluent, v_1 the volume fraction of the diluent, and χ_1 a thermodynamic interaction parameter¹⁵, which can be written as $\chi_1 = BV_1/RT_m$, where B is the molar free energy change brought about by first-neighbor interactions. A form of Equation 1 more

convenient for the analysis of experimental data is:

$$[1/T_m - 1/T_m^0]/v_1 = (R/\Delta H_u)(V_u/V_1) \left[1 - \left(\frac{BV_1}{R} \right) v_1/T_m \right] \quad (2)$$

Thus, from measurements of the melting temperature as a function of diluent concentration, there can be obtained the value of ΔH_u , one of the fundamental molecular parameters of crystalline polymers and one of great utility.

The melting temperatures of mixtures of the purified rubber hydrocarbon with each of the three diluents were determined dilatometrically. The heating rates employed were similar to those described for the pure polymers, and similar variations of the volume with time were observed. The crystallization was induced by maintaining the original amorphous mixtures at temperatures

TABLE II
MELTING TEMPERATURES OF NATURAL RUBBER-DILUENT MIXTURES

v_1	T_m (° C)	ΔH_u cal./mole of repeating unit ^a	BV_1/R
With tetradecane			
0.122	17	1040 ± 80	1.07
.153	16		
.215	14-15		
.240	13		
.288	11-12		
.296	11		
.394	7-8		
With methyl oleate			
0.157	17-18	980 ± 30	1.49
.170	16-17		
.210	16-17		
.292	14		
.297	13-14		
.364	11-12		
.370	12-13		
With dodecane			
0.165	15-16	1100 ± 60	1.18
.220	13-14		
.256	12-13		
.356	8-9		
.360	8-9		

^a The uncertainty in ΔH_u is estimated from the intercepts of the slightly different straight lines to which the data in Figure 2 can be fitted.

where the crystallization rate was comparable to that of the bulk rubber at 0°, so that appreciable crystallization developed after 48 hours. Because of the lengthy time intervals required, it is quite impractical to conduct the crystallization at temperatures more conducive to the formation of the most perfect crystallites. To correspond with actual experimental conditions, T_m^0 was, therefore, approximated by 296° K (23° C) for these studies, which introduces a slight error in the subsequent analysis. The melting temperatures of the mixtures, which covered a range of concentrations from about $v_1 = 0.10$ to 0.40, are given in Table II. In Figure 2, as suggested by Equation 2, $(1/T_m - 1/T_m^0)/v_1$ is plotted against V_1/T_m for each of the diluents used.

The data of Figure 2 can be represented by straight lines, and from the slopes and intercepts of the plots ΔH_u and BV_1/R are obtained; these values are

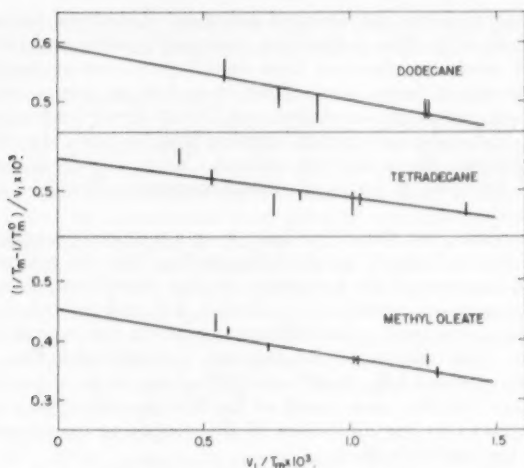


FIG. 2.—Plot of $(1/T_m - 1/T_m^0)/v_1$ vs. v_1/T_m for natural rubber mixed with the indicated diluents.

also given in Table II. Employing these parameters and making use of Equation 1, the dependence of T_m on composition can be computed; these calculated results are represented in Figure 3 by the solid lines. The plotted points represent the experimental observations, and good agreement is achieved. The deviations from linearity observed in Figure 2 are merely reflections of the extreme sensitivity of this type plot when the depressions of T_m^0 are small. Concordant values of ΔH_u are obtained as expected, since it is a property of the repeating unit and is independent of the nature of the diluent or its interaction with polymer. The average value of ΔH_u is 1040 ± 35 cal. per mole of re-

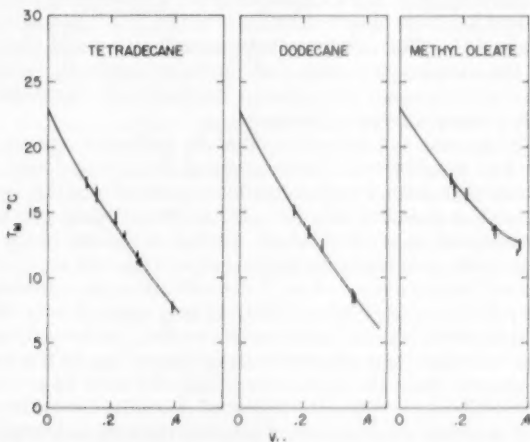


FIG. 3.—Plot of melting temperature, T_m , of natural rubber-diluent mixtures against volume fraction of diluent, v_1 . Solid lines are calculated.

peating unit, or 15.3 cal. per gram of polymer. If natural rubber could be made completely crystalline, a situation presumably never realizable, the heat of fusion that would be observed from calorimetric measurements would be ΔH_u . The entropy of fusion is calculated to be 3.46 cal. per repeating unit, or 1.15 cal. per deg. per single bond that can "rotate freely" when in the amorphous state. This value is somewhat smaller than has been observed for other polymers¹⁴; however, this is not too rational a basis of comparison, since at a minimum the entropies of fusion of various polymers should be compared at constant volume.

The value of ΔH_u can also be obtained from appropriate experiments where the crystallization is induced by stretching rather than by cooling. If T_m is measured as a function of the elongation at high elongation, then by the application of an equation developed by Flory¹⁶, ΔH_u can be deduced. Experiments of this type are much more difficult to perform and interpret than those reported here. The results of Arlman and Toppel¹⁷ and Fox, Flory and Marshall¹⁸ give values of ΔH_u of 1030 and 800 cal. per mole, respectively, which are in fair accord with the value based on the diluent studies, particularly when due regard is given to the difficulties of the stretching experiments and the differences in the materials used.

The volume change per repeating unit on melting, ΔV_u , can be estimated for natural rubber from data available in the literature. The specific volume of the completely amorphous polymer is given by Wood and Bekkedahl⁶ as 1.099 cm.³/g. at 28°. Bunn¹⁹ and Fisher²⁰ have reported a value of 1.00 g./cm.³ as the density of the unit cell of the rubber crystallites at 20°. At 28° the specific volume of the crystal can be estimated quite accurately to be 1.001 cm.³/g. by assuming that the rate of change of specific volume with temperature is 2×10^{-4} cm.³/g./deg.²¹. ΔV_u then is 0.098 cm.³/g. The variation of the melting temperature with applied hydrostatic pressure, P , is given by the Clapeyron equation as:

$$dT_m^0/dP = T_m^0 \Delta V_u / \Delta H_u = 0.0465 \text{ deg./atm.} \quad (3)$$

when T_m^0 is taken as 301° K at 1 atmosphere. The melting temperature at 1230 atmospheres has been observed by Dow²² to be 77.5°, and calculated from Equation 3 to be 84°. The difference between calculated and observed is certainly within the experimental error and illustrates again the validity of the application of thermodynamic principles to the melting of crystalline polymers, in this case for a one component system.

Polymers in general and natural rubber in particular are only partially crystalline even at equilibrium. Since many of the physical and mechanical properties of polymers depend on the amount of crystallinity it is quite important to determine this quantity reliably. It has been already pointed out that on heating, subsequent to crystallization, marked variations of the amount of crystallinity occur in polymeric materials before apparent equilibrium is attained at a given temperature. Also if crystallization is occurring from the supercooled liquid the rate of crystallization, and consequently the time for the equilibrium degree of crystallization to be attained, is extremely temperature sensitive²³, and can vary from minutes to days, depending on the temperature. Thus any statements about the degree of crystallinity must be accompanied by a definite thermal history. Since the degree of crystallinity can be determined by a variety of methods, if a comparison between the different methods is to be made, it is of the utmost importance that the polymer receive the same thermal history. Prior to the measurement of the degree of crystallinity of natural

rubber, a convenient thermal history to follow is that of crystallization from the supercooled liquid at 0° for a sufficient period of time so that equilibrium is practically attained.

For natural rubber which had received this thermal treatment, Bekkedahl and Matheson²⁴ found that the heat of fusion as determined calorimetrically, ΔH^*_u , is 4.00 cal./g. Since ΔH_u , the heat of fusion per repeating unit, has been determined from the present work to be 15.3 cal./g., the ratio $\Delta H^*_u/\Delta H_u$ is equal to 0.262; this is the fraction of the material that is crystalline. This quantity can also be determined from density measurements, since λ , the degree of crystallinity, is equal to the ratio $(\bar{V}_a - \bar{V})/(\bar{V}_a - \bar{V}_c)$, where \bar{V}_a is the specific volume of the amorphous or liquid polymer at the temperature under consideration, \bar{V}_c the specific volume of the all-crystalline polymer at this temperature, and \bar{V} the specific volume of the semicrystalline polymer. At 0°, \bar{V}_a and \bar{V} are 1.080 and 1.054 cm.³/g., respectively⁴; a value at 0° of \bar{V}_c of 0.996 cm.³/g. is determined from the density of the crystal unit cell²⁵, assuming that $d\bar{V}_c/dT$ is 2×10^{-4} cm.³/g./deg. C. The degree of crystallinity is then calculated to be 0.31 ± 0.04 .

The rate of change of specific volume with temperature of a substance in the glassy state $d\bar{V}_g/dT$ is known to be the same as $d\bar{V}_c/dT$, the rate of change of specific volume with temperature of a substance in the crystalline state²⁶. It would be expected, then, that for natural rubber $d\bar{V}_g/dT$ would be independent of the degree of crystallinity and equal to $d\bar{V}_c/dT$. It has been verified by Bekkedahl²⁴ and by Work²⁷ that $d\bar{V}_g/dT$ for natural rubber is independent of the degree of crystallinity. Thus λ should equal the ratio of $(d\bar{V}_a/dT - d\bar{V}/dT)/d\bar{V}_a/dT - d\bar{V}_g/dT$. From Bekkedahl's work it is found that $d\bar{V}_a/dT$ equals 7.42×10^{-4} cm.³/g./deg. C., $d\bar{V}/dT$ equals 5.72×10^{-4} cm.³/g./deg. C., and $d\bar{V}_c/dT$ equals 2×10^{-4} cm.³/g./deg. C., so that λ becomes equal to 0.31 ± 0.04 .

These independent methods give excellent agreement for the fraction of the natural rubber which is crystalline, and are in accord with the much earlier estimates of Parks²⁸. Determinations of the degree of crystallinity by means of x-ray methods are unfortunately not available for natural rubber undergoing the specified thermal treatment. However, from the work of Goppel and Arlman²⁹ on unstretched natural rubber, it can be reliably estimated that the degree of crystallinity resulting from the specified thermal treatment would be about 0.30 to 0.35. Thus, good agreement is obtained for the degree of crystallinity of natural rubber, regardless of the method used in its determination. This appears not to be the case for some other polymers, notably polyethylene³⁰, which has been extensively studied. However, for any rational comparison to be made, the same thermal history must be maintained, and it is not at all clear that this has been done for the other polymers investigated.

An expression for the retractive force f of stretched vulcanized (cross-linked) natural rubber can be given from general thermodynamic considerations as³¹:

$$f = (\partial E/\partial L)_{T, v} + T(\partial f/\partial T)_{p, \alpha} \quad (4)$$

where

$$(\partial f/\partial T)_{p, \alpha} = -(\partial S/\partial L)_{T, v}$$

and E is the internal energy, S the entropy, L the stretched length, and α the ratio of the stretched to the unstretched length at the given temperature. By maintaining the pressure p and the elongation α constant and determining the variation of the retractive force with temperature, the contributions to the

retractive force of both the internal energy changes and the entropy changes can be assessed.

It is found²² that up to elongations of about 200 to 300 per cent ($\alpha = 3-4$), $(\partial E/\partial L)_{T,V}$ is effectively equal to zero, so that the change of entropy with length of the entire amorphous material is entirely responsible for the retractive force. At slightly higher elongations $(\partial E/\partial L)_{T,V}$ begins to decrease very rapidly and assumes large negative values on subsequent elongations. It is well known from x-ray²³ and density²⁴ measurements that this is a region where the crystallization of rubber commences. The isothermal stress-strain curve at this point shows an abrupt and continual rise due to the accelerated decrease of entropy with length on further elongation¹⁶.

The total internal energy change ΔE in stretching the rubber from $\alpha = 1$ to a given elongation α can be obtained, as has been indicated by Boonstra²⁵, by graphically determining the value of

$$\int_{\alpha=1}^{\alpha} (\partial E/\partial L)_{T,V} d\alpha$$

Boonstra²⁵ suggested that if the decrease of internal energy on stretching were due entirely to crystallization, the ratio of $\Delta E/\Delta H_u$ should equal the fraction of the crystalline material. Using a value of ΔH_u determined in a somewhat arbitrary manner, though remarkably close to the value reported here, he was able to demonstrate that almost all the internal energy change was indeed due to crystallization. The results of repeating the calculations based on Boonstra's original data but using ΔH_u equal to 15.3 cal./g. are given in Table III. Two

TABLE III
DEGREE OF CRYSTALLINITY OF NATURAL RUBBER ON
STRETCHING (FROM BOONSTRA)²⁵

$\Delta H_u = 15.3$ cal./g. of unit.

Elongation:	$\frac{\Delta E}{\text{cal./g.}}$	$\frac{300\%}{\Delta E/\Delta H_u}$	λ (x-ray)	$\frac{\Delta E}{\text{cal./g.}}$	$\frac{400\%}{\Delta E/\Delta H_u}$	λ (x-ray)	$\frac{\Delta E}{\text{cal./g.}}$	$\frac{500\%}{\Delta E/\Delta H_u}$	λ (x-ray)
Sample S	0.394	0.026	0.04	1.845	0.12	0.15	3.46	0.23	0.30
Sample T	.398	.026	.05	1.44	.095	.105	2.93	.19	0.19-0.22

different rubber vulcanizates, designated as sample S and T, respectively, were used, and the degree of crystallinity was independently determined by the x-ray method²⁹. Quantitative agreement is obtained between $\Delta E/\Delta H_u$ and the degree of crystallinity, which strongly suggests that the crystallization process is the cause of the large internal energy changes that are observed. This conclusion is based solely on a thermodynamic analysis of the experimental facts, without recourse to any molecular interpretation as to the nature of the retractive force. A quantitative molecular interpretation of the upsweep of the stress-strain curve which sets in at about $\alpha = 3$ naturally will have to take into account the phase change that is occurring. It cannot be explained solely on the basis of the entropy change that occurs in deforming a completely amorphous material²⁶.

SUMMARY

The existence of an equilibrium melting temperature, T_m° , at $28 \pm 1^\circ$, for unstretched natural rubber has been established, using dilatometric methods. The lower melting temperatures previously observed are a consequence of the low temperatures of crystallization and the rapid heating rates employed. From melting point studies of mixtures of the polymer with low molecular-

weight diluents, the heat of fusion per repeating unit, ΔH_u , has been evaluated as 15.3 ± 0.5 cal./g. The values of ΔH_u and T_m^0 have then been combined with data of other workers to obtain the following information concerning natural rubber: (1) The variation of melting temperature with applied hydrostatic pressure has been calculated from the Clapeyron equation to be $0.0465^\circ \text{C/atm}$. (2) The degree of crystallinity resulting from maintaining a sample at 0° until the rate of crystallization is negligible has been calculated, by three independent methods, to be in the range 26 to 31 per cent. (3) Analysis of the stress-strain-temperature relationship has indicated that crystallization is the cause of the large internal energy changes that are observed at relatively high elongations.

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X-RAY INVESTIGATION OF THE AMORPHOUS STATE OF RUBBER *

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The x-ray diffraction pattern of amorphous rubber, which is an amorphous ring, resembles the pattern of low-molecular liquids.

In our previous work¹, it was established that the diffraction pattern observed is due to the coherent scattering of only those segments of the molecular chains in which the aggregation is analogous to that of low-molecular liquids, and is determined by the presence of a pseudo-order. A large part of the links of the molecular chains, owing to the prevailing disorder, scatters the x-rays incoherently, like scattering by a gas.

For one component of amorphous rubber, the concept of "liquid phase" was introduced, and, for the other, that of "gaseous phase", thereby subdividing them according to the type of scattering of x-rays.

Amorphous rubber, according to our data, contains a large number of chain segments which are characterized by a high degree of disorder.

The presence of such a disordered molecular phase is a general and characteristic property of high-molecular substances, and is caused by natural obstacles in the dense packing of the large molecules. This characteristic of molecular aggregation is undoubtedly reflected in the physical-mechanical properties of polymers.

According to our theories, the reversible deformation of polymers, due chiefly to changes of shape of the molecules², is determined principally by the disordered molecular "gaseous" phase. When different polymers contain the same proportions of the disordered phase, the differences in the values of their elastic deformation are determined principally by the mobility of the molecular chains themselves. The high elasticity of rubber, which distinguishes it from other polymers, can, from this viewpoint, be explained by the great mobility of its molecular chains, which in turn is attributable to the relatively low value of the energy barrier of rotation around the individual intramolecular bonds.

In the irreversible plastic phase of deformation, which is related to the mutual displacement of large segments of the molecular chains, and whole molecules, the "liquid" phase of the amorphous polymer plays a fundamental role. The same obstacles in the dense molecular packing are responsible for the inability of high-molecular substances to crystallize completely. The principles underlying the nature of the aggregate state in amorphous polymers, as developed by the authors, have recently been confirmed by x-ray studies of other authors³. In the present article, new data which are presented indicate changes in the molecular aggregation of amorphous rubber as a function of temperature, as well as a result of heat treatment and fatigue by periodic deformation of natural rubber.

* Translated from RUBBER CHEMISTRY AND TECHNOLOGY from the *Khím. i Fiz.-Khím. Vysokomolekul. Soedinenii*, *Doklady 7-oi Konf. Vysokomolekul. Soedinenii*, 1962, pages 242-245.

TEMPERATURE RELATION OF THE PATTERN OF SCATTERING BY RUBBER

With a change of temperature of exposed specimens of amorphous rubber, characteristic changes are observed in their x-ray scattering patterns. Figure 1 shows curves of scattering of filtered copper radiation by natural rubber (smoked sheet) at temperatures of 20°, 80°, and 120° C.

Three x-ray patterns of each sample of rubber were taken in a specially designed chamber, with a standard control substance: the first at room temperature, the second at an elevated or at a reduced temperature, and the third also at room temperature. In this way the reversibility of the temperature effect of scattering was established, and conditions were assured for a scattering pattern of the same exposed portion of the specimen.

Comparison of the intensity curves shows that, with a rise of temperature, the intensity increases sharply in the range of angles smaller than the angle of scattering corresponding to the maximum of the amorphous ring. The changes observed in the scattering patterns indicate molecular-structural changes in the amorphous rubber resulting from the temperature changes.

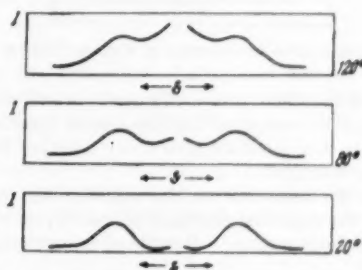


Fig. 1.—Curves of intensity of scattering by rubber at three different temperatures.

For the case described, of complete disorder in the relative distribution of the molecular chains of the rubber and links along the chains, the x-ray scattering pattern is characterized by the absence of interference maxima like scattering by a gas, where each link would act as a scattering unit.

A uniform steep rise of intensity in the range of small angles is characteristic of scattering by gases, while scattering by low-molecular liquids is characterized by the presence of interference maxima of scattering, due to the next neighbors in the molecular distribution and the fall of the intensity to near zero in the range of small angles.

The increase of intensity of scattering observed in this work in the range of angles smaller than those corresponding to the interference maximum during an increase of the temperature likewise attests to the increase of the disordered "gaseous" phase of the amorphous rubber. The increasing standardized intensity for any small scattering angle beyond the limits of the interference maximum can serve as a quantitative measure of the increase of the degree of molecular disorder; in other words, the amount of the "gaseous" phase of the amorphous rubber during an increase of temperature.

It is interesting to note the similarity of the observed temperature relation of the scattering pattern in rubber (Figure 2) to the changes in the scattering

pattern of low-molecular liquids in the critical temperature range⁴, as well as the scattering in condensed gases as related to pressure⁵.

Our measurements of rubber are compared, in Figure 2, with those of Nolle⁴, who studied the scattering of x-rays in diethyl ether when heated at temperatures higher than the critical temperature. With an increase of the temperature, the same increase of intensity in the small angle range is observed for ether as for rubber. Heating of ether above the critical temperature causes the interference maximum to disappear, and the intensity curve increases

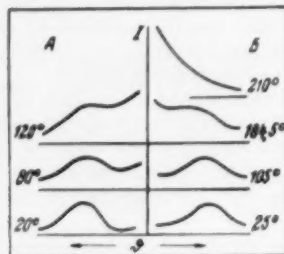


Fig. 2.—Experimental curves of scattering: A. Natural rubber; B. Diethyl ether.

steadily toward the small angles; this is a typical pattern of scattering by gases.

In connection with the changes of the disordered "gaseous" phase during an increase of temperature, the question also arises whether the "liquid" phase of the amorphous rubber changes.

Measurements of the intensity of the interference maximum at various temperatures confirm the expected decrease of the "liquid" phase of amorphous rubber during a rise of temperature. Results of measurements of the intensity

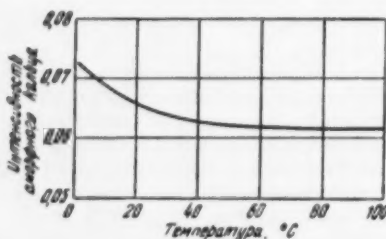


Fig. 3.—Intensity of the amorphous rubber ring as a function of the temperature. The ordinate represents the intensity of the amorphous ring; the abscissa the temperature in °C.

of the interference maximum according to its height with a large number of x-ray patterns taken with a standard substance, are shown in Figure 3. In order to assure obtaining a scattering pattern of the same exposed portion in a heated specimen and to control the reversibility at every temperature, three x-ray patterns were taken of each specimen: the first before heating, the second during heating, and the third after heating.

It should be pointed out that, during heating in air, oxidation of the rubber is unavoidable; this causes an increase of intensity of the interference maximum.

However, the control roentgenograms show that the effects of oxidation during the exposure of heated specimens are slight. Irreversible changes of intensity did not exceed 5 per cent, and were taken into account in the calculations.

CHANGE OF INTENSITY OF THE INTERFERENCE MAXIMUM DURING OXIDATION OF RUBBER

The relation between the "liquid" phase and "gaseous" phase in amorphous substances is quite variable, and depends on the chemical nature of the molecules, as well as on external factors.

In the preceding work¹, it was shown that, during the plasticization of rubber, which is accompanied by oxidation, the intensity of the interference maximum (amorphous ring) increases. It was interesting to study the changes of intensity of the interference maximum during direct and extensive oxidation of the rubber. We studied the change of intensity of the interference maximum in specimens of natural rubber heated in air for 20 hours at 100° C. Rubber thus treated becomes a sticky plastic resinous product. The results of the measurements show that the intensity of the interference maximum of such heat-treated specimens increases 15-20 per cent in comparison with that of corresponding untreated control specimens.

As is known, processes of intense oxidative destruction take place when rubber is heated in air, and these are accompanied by a fundamental change in the chemical nature of the molecular chains, and also by an increase of the proportion of the low-molecular fraction. At rupture, the degree of unsaturation in the molecular chain of the double bonds decreases, and the number of oxygen groups increases².

The increase of intensity of the interference maximum can be explained both by the increase of intermolecular forces resulting from the presence of oxygen groups, with consequent increase of the degree of molecular order, and also by an increase of the low-molecular fraction, which acts in the same sense.

The effect of increase of intensity of the interference maximum when vulcanized natural rubber is fatigued by repeated deformation was also observed. The magnitude of the change of intensity here is a function of the degree of fatigue. It is possible that another basic cause of the increase of intensity of the interference maximum in fatigued specimens are the oxidation processes which occur and which, as is known, are intensified during the mechanical deformation of rubber.

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MOLECULAR WEIGHTS OF EMULSION POLYDIENES *

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In the polymerization of dienes there is always the possibility of a cross-linking reaction between the polydiene chains because of the residual double bonds in the chains. Such a reaction can eventually lead to the formation of "infinite networks" which are characterized by loss of solubility (gel). The statistics¹, mechanism², and kinetics² of the formation of such networks during polymerization have been treated in recent years. From this treatment it becomes apparent that the onset of gel occurs when there is one cross-linked monomeric unit per weight-average primary chain. The latter term refers to the polymeric chain uncontaminated by any cross-links. Recent data³ have shown that the rate of the cross-linking reaction is relatively slow compared to the propagation reaction during a polymerization, and that polydiene chains can reach lengths of at least several thousand units without including a cross-linked unit. This permits the attainment of synthetic rubber of reasonably high molecular weight without the inclusion of an insoluble gel fraction.

The emulsion polymerization system, which is used so extensively in the synthetic rubber industry, is governed by special considerations, as regards both the cross-linking reaction and the factors controlling the chain length. Because the bulk of the polymerization occurs within the polymer particles, which are kept more or less saturated with monomer, their concentration remains relatively constant as long as any free monomer phase exists (50 to 60 per cent conversion). Hence, unlike the case of bulk polymerization, the rate of the cross-linking reaction (as well as that of the polymerization reaction) remains constant up to 50 to 60 per cent conversion. In other words, in emulsion systems, the cross-linking reaction proceeds at a uniform but faster rate than in bulk systems during the first half of the polymerization, owing to the higher concentration of polymer at the locus of reaction. Beyond that point, the cross-linking rate increases as the polymer concentration increases.

Under the above conditions, insoluble polymer networks are formed in emulsion systems if and when the molecular weight of the polydiene becomes sufficiently large to contain one cross-linked unit per weight-average chain, the frequency of cross-links remaining more or less constant up to 50 per cent conversion. The suppression of such networks is achieved in the synthetic rubber industry by means of "modifiers" or chain regulators which control the length of the polymer chain below the critical limit for gel formation. Such modifiers are chain-transfer agents, generally mercaptans (thiols), which are naturally depleted as the polymerization proceeds. In this way, the chain length in-

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creases with conversion until it reaches the critical size for gel formation, at which point the first network appears. Hence, up to 50 or 60 per cent conversion, it is this increase of chain length which eventually leads to the first sign of gel, the severity of the cross-linking reaction remaining constant. However, beyond 60 per cent conversion there appears the added factor of increasing polymer concentration, which actually increases the rate of the cross-linking reaction as well.

THE GEL POINT

The conversion at which the first insoluble polymer network makes its appearance is defined as the gel point. Beyond that point, the gel increases both in quantity and degree of cross-linking, as measured by its decreased swelling in

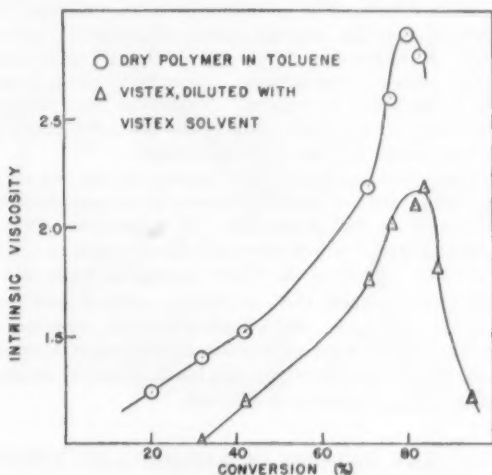


FIG. 1.—Intrinsic viscosity vs. conversion for GR-S at 50° C.⁴

solvents. Because the cross-linking reaction preferentially forms insoluble networks from the species of higher molecular weight, the average molecular weight of the soluble polymer decreases beyond the gel point. Thus, for instance, a plot of intrinsic viscosity against conversion generally reaches a peak at the gel point, followed by a continuous drop thereafter. A typical curve of this type, taken from a GR-S polymerization with the Mutual recipe, is shown in Figure 1. The rising portion of the curve is obviously due to the increasing chain length caused by depletion of the thiol and possibly by the cross-linking reaction as well. The occurrence of the peak and the subsequent decrease of viscosity have been discussed.

One complicating factor in observing the gel point arises because of the nature of emulsion polymerization. It is obvious that, in this type of polymerization, the infinite networks which are formed during the reaction cannot exceed the size of the latex particle (ca. 1000 Å. diameter). Such small particles of cross-linked polymer are referred to as microgel⁵. During coagulation and drying of the polymer, these netted particles may or may not be interlinked into

a visible (macrogel) network, depending on the type of treatment. Furthermore, the solubility of the polymer in a solvent may depend to a large extent on the possibility of redispersion of such microgel. Hence an accurate determination of gel is very difficult, when based on solubility measurements. This is especially true in the vicinity of the gel point, where the low frequency of cross-links in the network leads to a very tenuous structure, easily disrupted by solvents. On the other hand, attempts to interlink the microgel particles into a definite macrogel network by more drastic drying or heat treatment may actually lead to the cross-linking of otherwise soluble macromolecules. These factors render the sol-gel separation problem an extremely difficult one from a quantitative viewpoint.

To detect the presence of microgel, it is much simpler to avoid any treatment which may lead to the formation of macrogel, but, instead, to disperse the microgel in the solvent. The contribution of the microgel to the intrinsic viscosity is very low, since the network cannot experience much extension even in a good solvent. Furthermore, as it is the species of higher molecular weight that first form the microgel, the intrinsic viscosity of the polymer will show a noticeable drop if microgel is present. Therefore, the viscosity-conversion curve shows the same characteristic peak at the gel point as in Figure 1, which applies only to the soluble portion of the polymer.

The microgel may be dispersed in the solvent in one of two ways. In the Vistex technique⁵ the latex is dissolved directly in a compatible mixed solvent, e.g., benzene-isopropyl alcohol (80 to 20). In many cases similar results may be achieved by coagulating the polymer and dissolving it in a solvent immediately, without drying. Whereas the Vistex technique leads to a complete dispersion of the original microgel, the coagulation method may lead to a partial agglomeration of the microgel. Such agglomerations, whether visible or not, can usually be detected by filtering the solution through a coarse borosilicate glass frit⁶, because the fritted filter becomes blocked almost at once and will not permit the passage of any solution or solvent.

MOLECULAR WEIGHTS OF EMULSION POLYDIENES

The molecular-weight relationships during the process of emulsion polymerization of dienes are best illustrated by the viscosity-conversion curves, provided the mechanism controlling the chain length is known. The use of thiol modifiers as regulators of chain length makes it possible to determine chain lengths from the known mechanism of chain transfer. On the basis that one molecule of the thiol is consumed for every chain formed, it becomes possible to calculate the chain length during any period of polymerization from the known kinetics of thiol consumption. The latter have been studied for several different thiols in different monomer systems. In certain cases, the thiol is known to follow a first-order disappearance rate, at least during the first half of the polymerization reaction, and its rate of disappearance can be expressed as:

$$-dR/dP = rR \quad (1)$$

where R = thiol concentration, moles per mole of original monomer
 P = fractional extent of polymerization
 r = a constant

Under these conditions, the chain length can be calculated at any time during the polymerization, by means of the following relations:

$$\bar{n}_{ni} = 1/\tau R = e^{\tau P}/\tau R_0 \quad (2)$$

$$\bar{n}_{nc} = P/(R_0 - R) = P/R_0(1 - e^{-\tau P}) \quad (3)$$

where \bar{n}_{ni} = increment number-average degree of polymerization
 \bar{n}_{nc} = cumulative number-average degree of polymerization
 R_0 = initial thiol concentration

It is obvious from the above considerations that the chain length increases continuously during the polymerization, as the thiol is consumed. The initial chain length is, of course, a function of R_0 and τ while the rate of increase of

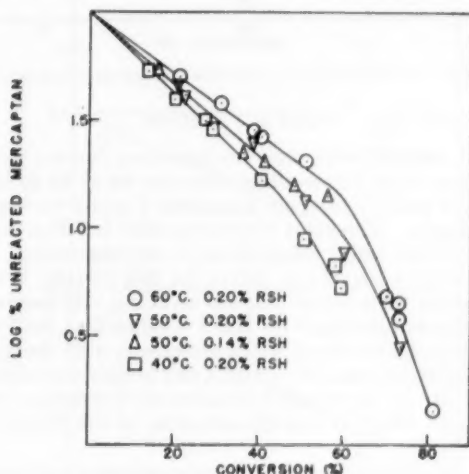


Fig. 2.—Mercaptan (thiol) disappearance in butadiene polymerization.

chain length is a direct function of τ . This increasing chain length is reflected in the viscosity-conversion curves for these systems. However, the above equations actually yield values only for the primary chain length, the actual chain length being greater because of the effect of the cross-linking reaction. As the intrinsic viscosity is much more sensitive to the higher molecular weights, the cross-linking of the longer chains can be expected to have a marked effect on the viscosity, leading to a marked rise of the viscosity-conversion curve up to the gel point. Some idea of the effect of the cross-linking reaction in distorting the distribution of molecular weights can be obtained by comparing the viscosity-average molecular weight with the calculated number-average primary molecular weight.

Three of the better known dienes have been studied in this fashion: butadiene, isoprene, and chloroprene. All the studies were made with emulsion polymerization in small bottles (4- or 8-ounce), using the Mutual recipe with Sulfole thiol. Details of the techniques and recipes have been described⁷.

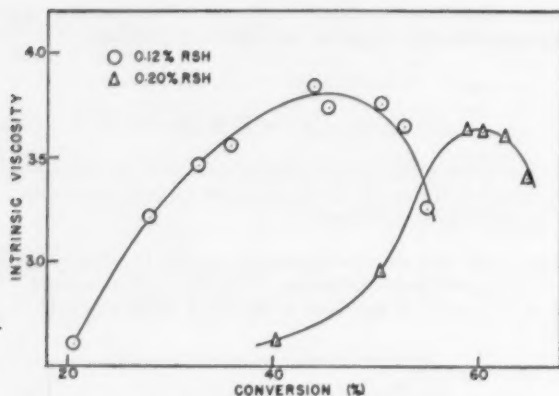


Fig. 3.—Intrinsic viscosity vs. conversion for polybutadiene at 40° C.

POLYBUTADIENE

Typical thiol disappearance plots for butadiene polymerization are shown in Figure 2. These plots follow a first-order law up to 40 to 50 per cent conversion, making it possible to apply Equations 2 and 3 for the calculation of primary chain lengths. The value of r for this thiol is 3.26 at 60° C, showing a small increase with decreasing temperature of polymerization.

To obtain viscosity-conversion curves for this system, it is necessary to know how to prepare the required polymer solutions. It has been shown very clearly by Henderson and Legge⁴ for GR-S systems that the Vistex technique yields viscosity-conversion curves which correspond with those obtained using the soluble portion of dry polymer. Such a pair of curves are shown in Figure 1. The Vistex viscosity is, as expected, consistently lower than that of the dry polymer in benzene, but that is a characteristic of the Vistex solvent (80-20

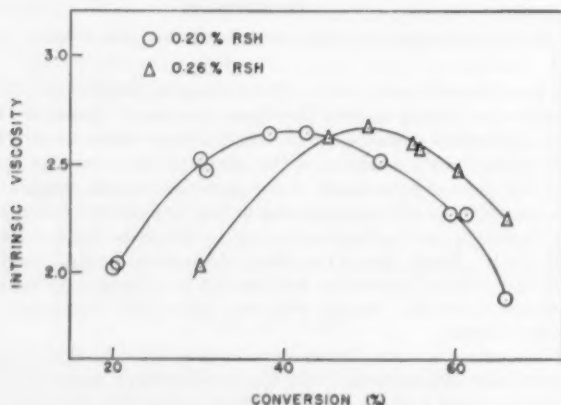


Fig. 4.—Intrinsic viscosity vs. conversion for polybutadiene at 60° C.

benzene-isopropyl alcohol). The position of the peak corresponding to the gel point is very similar for both curves. Hence it can be concluded that the Vistex method is applicable to polybutadiene systems.

The types of viscosity-conversion curves obtained with the Vistex method for polybutadiene are shown in Figures 3 and 4. For this work, the Vistex method was modified according to the suggestion of Henderson and Legge⁴ in that the solvent used for diluting the polymer solutions was benzene itself, so that the extrapolation to zero concentration simultaneously led to a value of the intrinsic viscosity in benzene alone. From this value it is, then, possible to calculate the viscosity-average molecular weight. It can be seen from

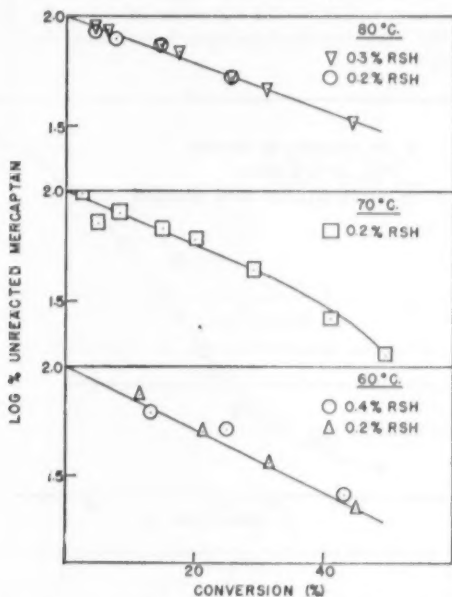


Fig. 5.—Mercaptan (thiol) disappearance in isoprene polymerization.

Figures 3 and 4 how the thiol charge affects the gel point at the two different temperatures, as expected, higher charges postponing the gel point to a higher conversion. However, regardless of the thiol charge, the intrinsic viscosity at the gel point seems to be a function of the polymerization temperature, lower temperatures leading to a higher peak in the viscosity curves. This means that the critical viscosity-average molecular weight prior to the gel point is higher for the lower polymerization temperature, a conclusion which is in agreement with the reduced rate of cross-linking at the lower temperature⁷.

POLYISOPRENE

The behavior of the same thiol in isoprene emulsion polymerization is shown in Figure 5. The disappearance rates are very similar to those found for butadiene, and follow a first-order law up to about 50 per cent conversion.

Therefore, the primary chain lengths might be expected to be similar to those obtained for the polybutadiene under the same conditions.

In attempting to plot viscosity-conversion curves for polyisoprene, however, some unexpected features are encountered. This is illustrated in Figure 6, where Vistex viscosity is compared with that obtained on solutions of the dry polymer in benzene. In this case, too, the Vistex method was used with benzene dilutions, so that the intrinsic viscosities should represent the true values in benzene. The agreement between the two viscosity methods is very good. However, the dry polymer suddenly shows the presence of gel at conversions above 47 per cent, whereas no peak occurs in the Vistex curve. Apparently the drying of the coagulated polymer (24 hours at 50° C at 1-mm. pressure) has been responsible for the formation of gel in the polymer. Hence, for polyisoprene, the Vistex method appears desirable for the study of viscosity-conversion curves.

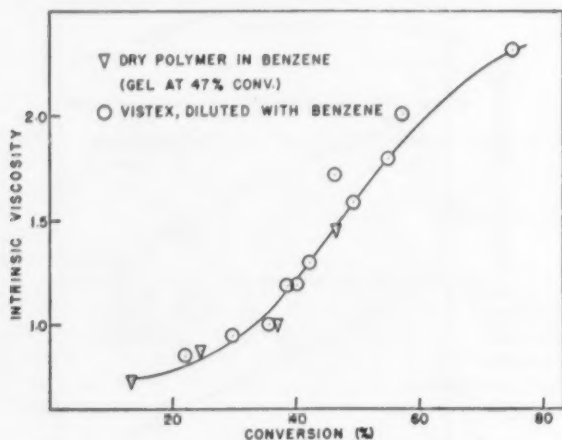


Fig. 6.—Intrinsic viscosity vs. conversion for polyisoprene at 60° C. 0.2% thiol

Such curves, obtained by means of the Vistex technique, are shown in Figures 7 and 8. Whereas the dry polymer had shown the presence of gel with a 0.2 per cent thiol charge at 60° C, an actual gel-point peak was not obtained in the viscosity-conversion curve until the thiol had been reduced to 0.03 per cent at this temperature. The conclusion is obvious that the cross-linking reaction during isoprene polymerization is much slower than for butadiene, but that this may be obscured by subsequent cross-linking during drying of the polymer. Hence the gel point in isoprene polymerization can be reliably established only by the Vistex techniques.

For polyisoprene, too, the viscosity-conversion curves show a characteristic peak whose height depends on the polymerization temperature, lower temperatures giving higher peaks. This is in agreement with the expected increase of the cross-linking reaction at higher temperatures. At 80° C, the curve for the higher thiol charge actually shows a lower peak. This seems to contradict the principle of a critical molecular weight at the gel point, as previously found for polybutadiene. However, the gel point in this case occurs at a conversion of

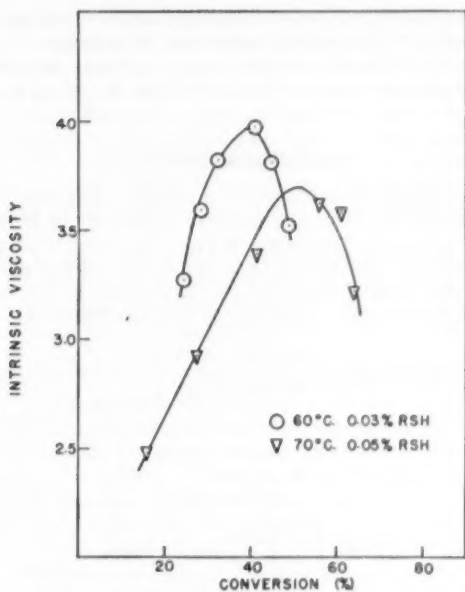


Fig. 7.—Intrinsic viscosity vs. conversion for polyisoprene.

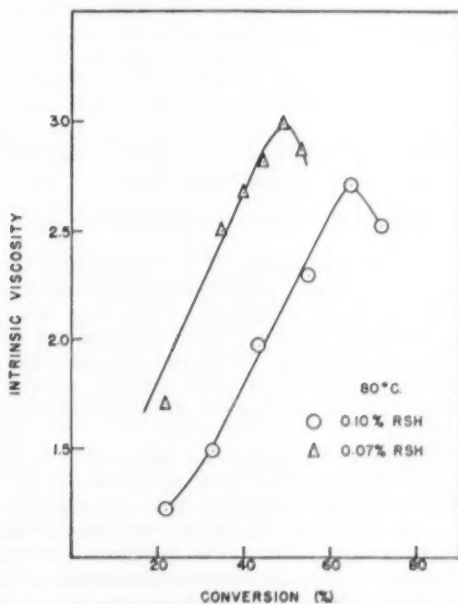


Fig. 8.—Intrinsic viscosity vs. conversion for polyisoprene.

about 65 per cent which is well beyond the region of constant monomer-polymer ratio. Hence, with the increasing proportion of polymer at this stage, the cross-linking rate should accelerate and lead to gelation at a lower molecular weight. The significance of the molecular weights at the gel point is discussed in a later section.

POLYCHLOROPRENE

Although the mechanism and kinetics of emulsion polymerization have been fairly well established for such hydrocarbon monomers as butadiene and isoprene⁸, relatively little such information is available about chloroprene. Recent work in this laboratory has shown that this very reactive monomer behaves differently from the other water-insoluble monomers, and actually resembles more the water-soluble types. Because of its great reactivity, it does not ad-

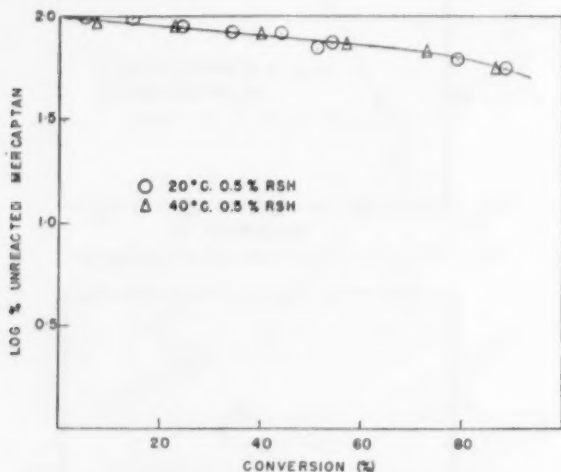


Fig. 9.—Mercaptan (thiol) disappearance in chloroprene polymerization.

here to the "ideal" kinetics as proposed by Smith and Ewart⁹. Unlike the usual water-insoluble monomers, polychloroprene particles are not formed exclusively from the monomer solubilized in the soap micelles. Hence the formation of latex particles is more rapid and continues for a longer period of time in chloroprene polymerization. It is, therefore, not safe to assume that the bulk of the polymerization occurs in the polymer particles saturated with monomer, and the mechanism may be very different from that described here for the other two dienes.

Despite these differences, it is of great interest to note the molecular-weight relationships which apply during the emulsion polymerization of chloroprene. Sulfole thiol behaves in the expected fashion as a chain regulator for polychloroprene too. Typical disappearance curves for this thiol are shown in Figure 9 for polymerizations at 20° and 40° C. It is obvious at once that the disappearance rate is much slower in the case of chloroprene than for butadiene or isoprene, the r values being only 0.50. The first-order rate of disappearance is

maintained up to about 80 per cent conversion and changes only slightly beyond that point. This means that even at 80 per cent conversion only about 30 per cent of the thiol has been consumed. Such a slow rate of disappearance should result in a lesser spread of the molecular-weight distribution curve, the average primary chain length varying only slightly during the polymerization. Furthermore, the thiol disappearance rate does not change with temperature, unlike the other dienes which both showed a slower thiol disappearance rate (relative) at higher temperatures. Apparently the activation energies of the transfer and propagation reactions are very similar for chloroprene and this thiol.

The influence of the thiol on the molecular weight of the polychloroprene can be observed from the viscosity-conversion curves as illustrated in Figures 10 and 11. The intrinsic viscosities shown in these figures were obtained on solutions of the solid polymer in benzene, and not by means of the Vistex technique used for the polybutadiene and polyisoprene. The polychloroprene behaved in an entirely different fashion than either of the other two dienes. Thus the coagulation of the polychloroprene latex in methanol apparently did not necessarily agglomerate the microgel, as freshly coagulated polymer "dissolved" in benzene, even when all the signs of microgel were present, e.g., turbidity and decreased viscosity of solution. However, standing at room temperature, or drying (even under vacuum) at elevated temperatures, led to the formation of visible macrogel in the polymer. The solutions prepared from freshly coagulated polymer generally passed through a coarse borosilicate glass frit, which is ordinarily very sensitive to plugging by microgel. Apparently the polychloroprene microgel is dispersed in a sufficiently fine state to pass through the filter. However, with increasing conversion (past the viscosity peak), the benzene solutions became increasingly difficult to filter (despite their lower viscosity) until a point was reached where the solution no longer passed through the frit. It is apparent that the amount and degree of cross-linking of the microgel are factors in its filterability through the frit, probably because of their effect on the aggregating properties of microgel particles.

The viscosity-conversion curves in Figures 10 and 11 are very illustrative. In view of the slow disappearance rate of the thiol regulator, it might be expected that the viscosity-conversion curve would be relatively flat, except as and where the cross-linking reaction might alter the molecular weight distribution, or lead to microgel. Thus at 20° C, and 0.5 per cent thiol, the viscosity-conversion curve is flat, as the cross-linking reaction is apparently not severe enough for a noticeable effect. However, at the same temperature but with lower thiol charges, a noticeable downward curvature is evident; apparently the cross-linking effect becomes more important as the higher molecular weights. The decrease in intrinsic viscosity is taken to be due to the formation of microgel. A similar trend is apparent in the 40° C polymerizations. Thus, with 0.8 per cent thiol, a relatively flat curve is obtained, but with 0.5 per cent thiol, the effect of the cross-linking reaction is very noticeable in leading first to a slight increase of the viscosity, followed by a sharp decrease as microgel is formed. The fact that higher levels of thiol are necessary for a given viscosity polymer at 40° C is obviously due not to any difference in thiol disappearance rate, but to the increased cross-linking reaction.

What is perhaps the greatest difference between the viscosity-conversion curves for polychloroprene and those of the other two dienes is the absence of well-defined peaks in the former. The only curve which shows the presence

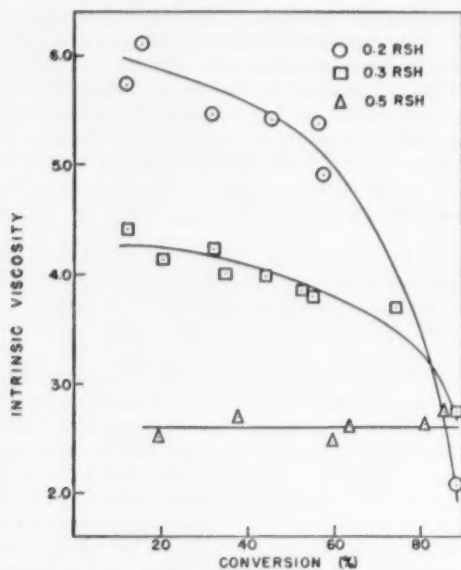


Fig. 10.—Intrinsic viscosity vs. conversion for polychloroprene at 20° C.

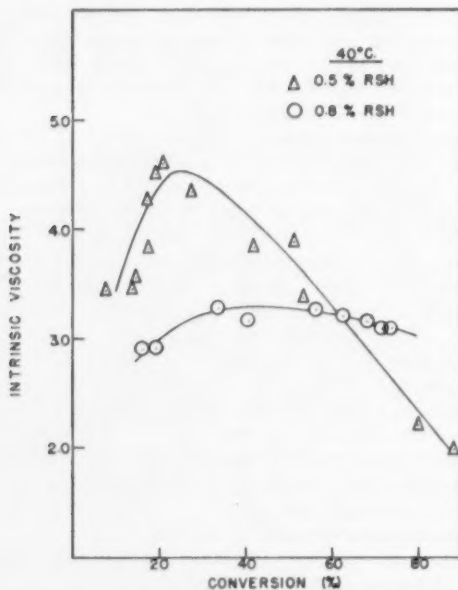


Fig. 11.—Intrinsic viscosity vs. conversion for polychloroprene.

of a decided peak is that of the 40° C polymerization with 0.5 per cent thiol. In the other curves, the absence of a peak can be explained by the relatively uniform average primary chain length formed because of the slow disappearance of thiol. However, if the primary chain length is sufficiently high, the cross-linking reaction becomes noticeable, and the viscosity curve shows a drop as more and more microgel is formed. As expected, this cross-linking reaction is most noticeable at 40° C, where it is severe enough to show up as a peak in the viscosity curve.

The significance of these intrinsic viscosity values in terms of molecular weight can be observed in Table I, where osmotic molecular weights and viscosities are compared. In addition, the molecular weights obtained by osmotic pressure measurements are compared with the calculated values (Equation 3) based on the kinetics of thiol chain transfer.

In the 20° C polymerization, the osmotic molecular weights are of the same order of magnitude as the predicted values, although considerably higher. This would be due, at least partly, to the effect of the cross-linking reaction,

TABLE I
OSMOTIC MOLECULAR WEIGHTS OF POLYCHLOROPRENE

Polymerization temp. (° C)	20	20	40	40
Thiol charge (% of monomer)	0.50	0.50	0.50	0.5
R_0 , moles/mole monomer $\times 10^3$	2.3	2.3	2.3	2.3
r	0.5	0.5	0.5	0.5
Conversion (%)	12.2	63.0	14.6	81.3
\bar{M}_{nc} (Equation 3)	80,000	90,000	80,000	94,000
\bar{M}_n (osmotic)	180,000	190,000	340,000 ^a	820,000 ^b
Intrinsic viscosity	2.40	2.54	3.56	1.80

^a $\pm 67,000$.

^b $\pm 204,000$.

but may also be due to some passage of low molecular-weight polymer through the membrane. At any rate, the action of the thiol as chain-transfer agent is certainly corroborated.

The molecular weights of the 40° C polymer, however, offer even more striking evidence of the occurrence of the cross-linking reaction. Thus, the osmotic molecular weights are much higher than predicted, and this effect is enhanced at higher conversion. Furthermore, the markedly lower viscosity of the high-conversion polymer is definitely not due to any decrease of molecular weight, but reflects instead the formation of microgel particles, which would not contribute much to the intrinsic viscosity. These data, therefore, offer unmistakable proof that the decrease of viscosity is due to microgel formation.

MOLECULAR WEIGHT DISTRIBUTION

Under conditions where a chain-transfer agent, such as Sulfolene thiol, plays the dominant role in controlling the molecular weight of the polymer, it is possible to predict the molecular-weight distribution from the known kinetics of chain transfer. Such distribution functions have been treated by Bardwell and Winkler¹⁰, who have shown how the molecular-weight distribution can be expected to change during the course of the polymerization because of depletion of the thiol. As a criterion of the molecular-weight distribution, they used the "heterogeneity index", i.e., the ratio of the cumulative weight-average chain length, \bar{n}_{wc} , to the cumulative number-average chain length, \bar{n}_{nc} . In the case of

a thiol-controlled polymerization where Equation 1 applies, the heterogeneity index was found to have the following form:

$$n_w/n_n = 2(e^{rP} - 1)(1 - e^{-rP})/r^2P^2 \quad (4)$$

This expression is independent of the actual concentration of thiol used. This heterogeneity index does not undergo very much change during the polymerization reaction, at least not until the thiol is almost completely depleted. Thus, with an r value of about 3, the heterogeneity index at 50 per cent conversion rises to 2.40 (from the original value of 2 based on probability), while at 80 per cent conversion it rises to a value of 3.2. When the r value is lower, e.g., 0.5, as in the case of the above chloroprene polymerizations—the heterogeneity index shows even less change, reaching a value of 2.01 at 50 per cent conversion, and only 2.03 at 90 per cent conversion. This means that the molecular-weight distribution of the polychloroprene would remain unchanged, to all intents, up to the highest conversions.

However, over and above this effect of the thiol chain-transfer agent on the molecular weight of the polymer, there is superimposed the effect of the cross-linking reaction. The general effect of the latter would be to interlink long chains into networks until sufficient such networks are formed to result in an infinite network, i.e., gel. Prior to the gel point, then, the effect of the cross-linking reaction would be to distort the molecular-weight distribution curve toward the higher values. Because of the relatively low frequency of cross-links required in the polymer chains for formation of an infinite network, the net effect would be the progressive formation of species of higher molecular weight, rather than the formation of highly branched chains. This shift of the molecular-weight distribution curve would be reflected in a rise of intrinsic viscosity of the whole polymer, since the latter measurement would be very sensitive to the species of higher molecular weight. This condition would apply up to the gel point, following which the intrinsic viscosity would decrease owing to the removal of the gel fraction from the solution (as either insoluble macrogel or dispersed microgel).

The effect of the cross-linking reaction in distorting the molecular-weight distribution curve can be determined by a comparison of the weight-average and number-average molecular weights. A very simple approach to this comparison would be to compare the intrinsic viscosity with the primary chain length, as calculated from thiol chain-transfer activity. This would have to be done prior to the gel point, as the intrinsic viscosity would decrease beyond that point. Obviously, the intrinsic viscosity at the gel point itself would show the maximum effect of the cross-linking reaction on the molecular weight.

Such a comparison is made in Table II for all three polydienes.

TABLE II
MOLECULAR WEIGHTS OF EMULSION POLYDIENES

Monomer	Isoprene	Butadiene	Chloroprene
Polymerization temp. (°C)	60	60	40
Thiol charge (% of monomer)	0.03	0.20	0.50
R_s , moles/mole monomer $\times 10^4$	0.87	5.8	23
r	3.32	3.26	0.50
Gel point conversion (%)	40	40	30
\bar{M}_w at gel point*	425,000	51,000	83,000
\bar{M}_n at gel point	670,000	513,000	1,790,000
\bar{M}_w/\bar{M}_n	1.53	10	21.6

* Cumulative number-average primary molecular weight as calculated from Equation 3.

The values for the viscosity-average molecular weights, \bar{M}_v , were calculated by means of the following equations, available in the literature:

$$\begin{aligned}\text{Polybutadiene (8)} \quad [\eta] &= 72.5 \times 10^{-4} \bar{M}_v^{0.48} \\ \text{Polychloroprene (9)} \quad [\eta] &= 1.55 \times 10^{-4} \bar{M}_v^{0.71} \\ \text{Polyisoprene} \quad [\eta] &= 5.0 \times 10^{-4} \bar{M}_v^{0.67}\end{aligned}$$

Unfortunately, no molecular-weight equations are available for synthetic polyisoprene in benzene solution. Hence the equation which applies to natural rubber in benzene¹¹ was used as the closest approximation, although the difference of chain structure between the two polymers is considerable. The use of these viscosity-molecular weight equations for polydienes is generally not too reliable, since different equations have to be used, depending on the polymerization temperature and even the degree of conversion. The above equations represent the closest approach possible in each case.

It can be seen from Table II that the ratio \bar{M}_v/\bar{M}_{nc} increases markedly from isoprene to butadiene to chloroprene. The value of 1.53 for isoprene is questionable, as the most probable distribution would predict a value of 2 to 3. The anomalous low value is undoubtedly due to the error introduced by the use of the viscosity-molecular weight equation for natural rubber. However, it is at least obvious that the cross-linking reaction increases in severity from isoprene to chloroprene. It has been shown¹² that the cross-linking reaction is five to six times as severe in butadiene polymerization as in the case of isoprene. The above data confirm this and also show that the cross-linking reaction is even more severe in chloroprene polymerization. This is also evidenced by the sensitivity of the chloroprene polymers to gel formation which has been observed here.

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DEGRADATION OF HIGH POLYMERS. SCISSION REACTIONS IN THE OXIDATION OF GR-S IN SOLUTION

I. EXPERIMENTAL PART *

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INTRODUCTION

The aging and degradation of polymeric substances are a result of the action of oxygen, ozone, light, and heat¹. These agents cause reactions of two types, which proceed simultaneously but at the same time differ in character: (1) bridging, or the formation of cross-linkages between the spatial chains, and (2) scissions, i.e., cleavage of the chains.

The present work is limited to a study of the scission reactions. The chief difficulty involved in any study of this phenomenon lies in the fact that scission and bridging take place simultaneously and have opposite effects. The predominance of either one of these two reactions over the other depends on the conditions of aging and on the chemical structure of the polymer.

Mesrobian and Tobolsky² were able to distinguish the scission phenomenon by studying relaxation under continued tension, and then determining the total effect by measurements under intermittent tension. Another possible way to distinguish the scission reaction is to use relatively dilute solutions; the effect of dilution is to separate the polymer chains from one another and thereby reduce the probability of bridging. This latter procedure is the one that was employed in the present investigation. To study the degradation of GR-S, a technique was utilized, with which it was possible to determine simultaneously the double bonds, the oxygen consumed, the peroxides formed, and the scission reactions.

The sample used in these laboratory experiments on degradation was a piece of GR-S weighing 1 kilogram³. This GR-S had been prepared by copolymerization of 75 per cent by weight of butadiene and 25 per cent by weight of styrene. After extraction by acetone of the antioxidant which had been added during manufacture⁴ (500 cc. of acetone and 10 grams of finely divided GR-S), the sample was dissolved in toluene (10 g. in 500 cc.) and fractionated by precipitation by alcohol⁵.

The molecular weights of the fractions were determined viscometrically⁶, i.e., by an Ostwald viscometer, in a thermostat at 25° C. The relation between molecular weight and viscosity was derived by the method of Scott⁷, i.e., by the relation: $[\eta] = 5.25 \times 10^{-4} M^{\frac{1}{2}}$, where M is the molecular weight and $[\eta]$ is the intrinsic viscosity, as defined by Duclaux and Wollmann⁸, i.e., $[\eta] = \ln \eta_r / \gamma$ where γ is the concentration of the polymer in the solvent (in g. per liter) and

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Revue Générale du Caoutchouc*. Part I is in Vol. 30, No. 11, pages 819-824, November 1953. Part II is in Vol. 31, No. 6, pages 473-478, June 1954. This mémoire comprises the principal results of a thesis submitted to the University of Paris March 3, 1953.

η_r is the relative viscosity of the solution, based on that of the solvent (ratio of time of flow of the solution to the time of flow of the same volume of pure solvent).

The error entering into the measurement of the concentration, determined by evaporation of the solvent and weighing of the residue, is of the order of 0.4 per cent. The error in measuring the molecular weight, lying in the range of 2-25 per cent, varies with the molecular weight, according to the law:

$$dM/M = (1/[\eta])d[\eta].$$

Measurement of the molecular weight can be made by methods other than the viscometric method. For example, osmotic pressure, lowering of the freezing point, and vapor pressure measurements give the number-average molecular weight as the M_n value, while diffusion of light makes possible the determination of the molecular weight as weight M_w .

In order for the viscometric weight M_v to have the same value as M_n and M_w , it is necessary or advisable that all the molecules of the fraction have practically the same weight, or at least that the small molecular weights be compensated by very large molecular weights. It is, therefore, necessary to use narrow fractions of the polymer⁵.

SCISSIONS

A polymer molecule has undergone scission when the molecule has been severed into two fragments. These are manifestly identical only when this scission takes place at the middle of the molecule. The relation of the number of fragments l to the number of scissions C is expressed by the equation: $l = C + 1$. The l value can be determined by the ratio of the initial molecular weight M_0 to the molecular weight $M_n(t)$ of the product at time t after scission, with the condition that $M_n(t)$ represents the mean number molecular weight and that the fraction of molecular weight M_0 is homogeneous⁶. One can then write:

$$C = \frac{M_0}{M_n(t)} - 1$$

To determine C from the mean weight molecular weight M_n or from the viscometric molecular weight M_v of the degraded fraction, it is necessary to know the distribution functions in number and in weight.

We have constructed distribution curves of totally and partially degraded GR-S. They do not substantiate any of the statistical theories of the degradation of long-chain molecules. In all cases, the degraded products were more homogeneous than the theories would predict⁹. It must, therefore, be concluded that the degraded fractions are sufficiently homogeneous for the number of scissions to be measurable approximately by the relation: $C = (M_0/M_n) - 1$.

DETERMINATION OF DOUBLE BONDS

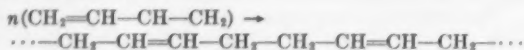
The determination of double bonds is indispensable in the study of degradation, for double bonds are responsible for the effects of oxygen on GR-S. It is possible to calculate a priori the number of double bonds in a chain of given molecular weight, on the strict condition that the polymer has undergone no chemical change which has caused a change of the degree of saturation.

Knowing the composition of the mixture used in the manufacture of GR-S (butadiene 75 g.-%, styrene 25 g.-%), the corresponding numbers of molecules

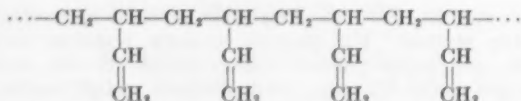
of monomer of each kind necessary to form 100 grams of copolymer can be calculated. These are 1.39 moles of butadiene and 0.24 mole of styrene.

The polymerization of butadiene can take place by two mechanisms:

(1) Addition at the 1,4-position:



(2) Addition at the 1,2-position:



Actually these two reactions proceed simultaneously. Kolthoff¹⁰ has established that, in GR-S polymerized in emulsion at 40° C, 20 ± 0.5 per cent of the double bonds are in the side chains. They result from 1,2-addition and do not even have the same reactivity as the double bonds of the main chain.

The double bonds of the benzene ring in styrene do not play any part in the degradation reactions, so we determined only the double bonds of the main chain, the number of which is, at the most, equal to the number of elementary chains in butadiene, irrespective of whether the polymerization process is at the 1,4-position or 1,2-position.

The method employed was that of Kemp and Peters¹¹, and consists of making iodine monochloride react on the double bonds and then determining the excess iodine monochloride by sodium thiosulfate in the presence of potassium iodide. We have made certain changes in this procedure, because of the fact that it is particularly designed for vulcanized rubber.

Instead of dissolving the polymer in *p*-dichlorobenzene at 200° C, which would have risked degradation of the GR-S, 5 cc. of a solution of 5 grams of GR-S in 1 liter of toluene was mixed at room temperature with a solution of 10 grams of *p*-dichlorobenzene in 5 cc. of chloroform. After addition of 5 cc. of iodine monochloride (0.2 *N* solution in carbon tetrachloride), the excess iodine monochloride was determined by the method indicated above. The total amount of iodine monochloride reacting with the solution was determined by a blank determination, which involved replacing in the above mixture the 5 cc. of solution of the polymer by 5 cc. of toluene. In this way, errors arising from any substitution reaction of the iodine monochloride with the toluene are avoided, a reaction which vitiates the results by an error of 3–5 per cent or even more.

This method gives results which are reproducible to about 5 per cent, and by it, the progressive disappearance of double bonds during the oxidation of GR-S in solution can be followed.

DETERMINATION OF PEROXIDES

The determination of peroxides is based on the method developed by Bolland and his collaborators¹². It involves, in principle, the oxidation of ferrous sulfate by peroxides and determination of the number of ferric ions formed.

We were obliged to change the ordinary technique because it is not applicable directly to GR-S, since this copolymer is not soluble in the methanol-benzene mixture used for natural rubber.

The reagent is a freshly prepared solution containing 0.1 cc. of 5 *N* sulfuric acid, 0.4 gram of Mohr salt, and 0.1 gram of ammonium thiocyanate in 20 cc. of methanol freed of oxygen by boiling. A mixture is made of 3 cc. of this reagent, 1 cc. of the polymer solution (5 grams per liter), and 16 cc. of toluene. The mixture turns red, and the intensity of the color, i.e., the absorption power, is measured by means of an electrophotometer, preferably standardized by a known solution of ferric chloride. This gives the total number of ferric ions formed: (1) from the peroxides formed in the polymer solution, and (2) from the oxygen dissolved in the toluene. The number of ferric ions formed by the latter process is determined by a direct experiment with pure toluene.

The value of this method has been demonstrated by means of a standard solution of benzoyl peroxide in toluene (0.05 gram per liter). The precision is 2-4 per cent.

DETERMINATION OF OXYGEN

We studied (1) the degradation of GR-S by oxidation under different pressures of oxygen, and (2) in certain cases, the rate of absorption of oxygen by the copolymer.

Determination of the oxygen present.—The degradation of GR-S in solution was studied in Pyrex tubes sealed to prevent evaporation of the solvent at high

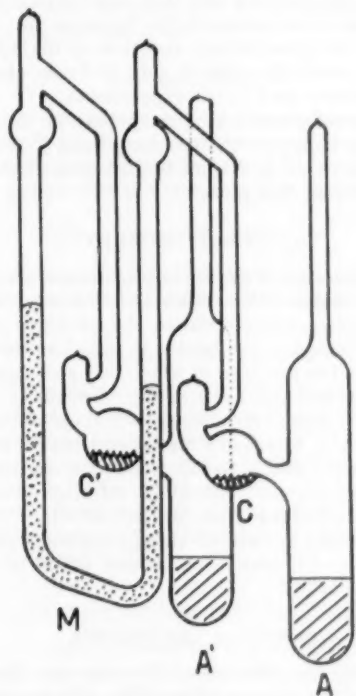


FIG. 1.—Differential manometer.

temperatures. Both ampoules and Ostwald viscometers were used. In the Ostwald viscometers, the upper two branches were joined into a single branch, which was sealed.

With a sealed viscometer, it is possible to measure the viscosity of the solution under any chosen pressure and at any desired temperature. The amount of oxygen present is determined by measuring the volume of the recipient. The amount of oxygen can be varied at will by sealing the viscometers under reduced pressure.

Determination of the oxygen absorbed.—Studies of the rate of absorption of oxygen have been the object of numerous investigations. The first measurements appear to have been those of Peachey¹³ in 1912. Later, Dufraisse¹⁴ measured the rate of absorption of oxygen by rubber by means of glass tubes connected to mercury manometers. This method was later utilized by van Amerongen¹⁵.

Other investigators found it preferable to study the rate of absorption of oxygen at constant pressure¹⁶, the oxygen required for oxidation being supplied during the reaction by electrolysis of an acid solution.

The apparatus used in the present investigation was a differential manometer, which consisted essentially of two sealed ampoules connected with each other by a U tube, containing the manometric liquid. One of the ampoules contained the solution of the polymer, the other contained pure solvent. The vapor pressure of the pure solvent was thus exerted equally on the two sides of the manometric tube, irrespective of the temperature. The difference between the pressure of the pure solvent and that of the polymer solution was disregarded because it was of the order of only 10^{-3} mm. of mercury at the concentration and temperature used in the experiments.

To prevent any gases formed during the oxidation (water, carbon dioxide, and formic acid)¹⁷ from changing the pressure, traps C of calcium oxide were placed between the ampoules A, A' and the manometric tube M of Figure 1. The manometric liquid was pure glycerol.

GENERAL METHOD

The kinetics of degradation were studied by determining simultaneously, as a function of time, the change of the number of double bonds, the scissions, the peroxides, and the oxygen consumed during the oxidation of GR-S in solution.

The solution to be degraded was heated in sealed ampoules immersed in an oil bath in an oven, the temperature of which was controlled to $\pm 1^\circ \text{C}$. The double bonds, scissions, and peroxides of the contents of each ampoule after heating for a prechosen time were determined simultaneously. The oxygen consumed was measured by means of a manometer heated in the same medium. With a viscometer it was possible to follow the degradation and to determine when the heating of an ampoule should be interrupted at any stage. The range of temperature studied was from 80° to 140°C .

This operating procedure has the advantage of giving simultaneous measurements of the rates of the different reactions and makes it possible to explain the mechanism of degradation.

EFFECT OF THE SOLVENT

In order to determine the influence of the nature of the solvent on the degradation, the curves of the changes of viscosity of a fraction dissolved in carbon tetrachloride and in toluene were compared. It was found that the change

of the viscosity for a fraction of mean molecular weight 100,000 as a function of the time of heating at 110° C was practically the same in the two solvents. All the experiments which will be described later were made with toluene as the solvent.

EFFECT OF CONCENTRATION

It was decided to study the scission reaction independent of bridge formation. Intermolecular bridges can form only if the polymeric molecules are sufficiently close to one another. There is, then, competition between bridge formation and scission, and the molecular weight of the degraded product should be higher than it would be if only scission took place. By a study of the differences of the molecular weights of a fraction degraded at different concentrations (1 to 10 grams per liter), it was proved that the molecular weight of the product degraded by an excess of air always has the same limiting value, irrespective of the concentration.

Therefore, at these dilutions, bridge formation is negligible. This result is explained by the fact that, since the bridge reaction is bimolecular with respect to the polymer molecule, dilution reduces considerably the probability of bridging. All further experiments were made with a concentration of 5 grams of polymer per liter of solvent, by which means the viscosities of the different fractions could be measured with good precision. Degradation at concentrations higher than 10 grams per liter could not be studied, since the viscosities of the solutions then became too great.

REPRODUCIBILITY

It was verified that the frequency of the measurements do not influence the degradation process. If heating of a polymer solution is interrupted, and the solution is let cool to room temperature, it will be found that the solution has the same viscosity, irrespective of the duration of the interruption.

EXPERIMENTAL RESULTS

The mechanism of degradation of GR-S was determined by a systematic study of each of the reactions capable of affecting scission of the polymer molecule.

THERMAL DEGRADATION

Diminution of the molecular weight of a polymer can be brought about either by the rupture of certain bonds, e.g., by oxidation, or by depolymerization. These two reactions may be simultaneous.

In order to ascertain the extent of the depolymerization reactions in the degradation of GR-S, a solution of this polymer was heated in vacuo. It was found that heat degradation is negligible up to 230° C, a result which confirms the data of Orr¹⁸ and Maderski¹⁹. Degradation by oxygen at temperatures below 200° was next studied.

DEGRADATION UNDER REDUCED PRESSURE

The dependence of degradation on the concentration of oxygen was studied with fractions of different molecular weights, viz., M_0 170,000, M_1 265,000, M_2 400,000, and M_3 450,000. The solutions were heated in sealed ampoules under different pressures for 10 hours at 110° C. By means of a sealed vis-

cometer, it was possible to tell when degradation was complete, i.e., when the viscosity no longer changed on continued heating. These experiments are recorded graphically in Figure 2.

For a given amount of oxygen, the fraction of double bonds ruptured is independent of the molecular weight when the latter is sufficiently high. With small amounts of oxygen, the scission reaction predominates over the oxidation reactions, and the amount of oxygen consumed for scission increases with the amount of oxygen present.

This result is not an isolated observation, e.g., Farmer and Sundralingam²⁰ have earlier noted that the number of atoms of oxygen absorbed per bond ruptured increases with the extent of oxidation.

If D_0 represents the total number of double bonds in the polymer molecule before degradation and C is the number of scissions per molecule of polymer, it will be found that the value of the ratio C/D_0 does not increase above a certain definite limit, $C/D_0 < 1/20$, irrespective of the amount of excess oxygen. This means that the molecular weight of a degraded fraction is never below 1000–1500, which corresponds to 20 elementary chain units of butadiene per molecule.

DEGRADATION BY OXYGEN IN EXCESS

The degradation of GR-S in solution is a complicated series of oxidation reactions. Oxygen attacks the double bonds, and this changes the degree of unsaturation of the polymer. The molecular weight decreases because certain bonds are ruptured, and this is manifest by peroxides in the reaction products. The experiments in the present work had for their purpose the determination of the relative extent of each of these reactions. Some of the experimental results have been published by Magat and the present author²¹. In this work, a probable relation was established between the amount of peroxides formed, as a function of the time of heating, and the change of molecular weight. This

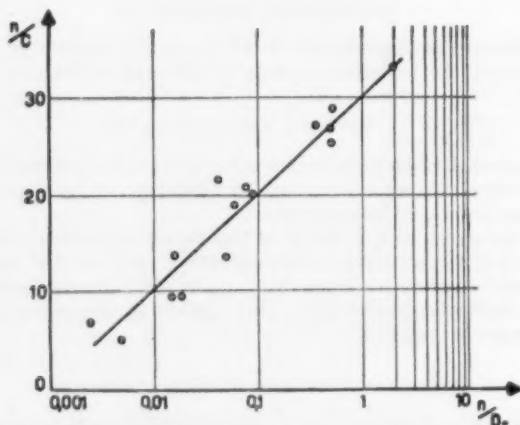


FIG. 2.—Degradation under different pressures. The number of molecules of oxygen required for one scission as a function of the number of oxygen molecules present per double bond. The abscissa scale is logarithmic. n —Number of oxygen molecules per molecule of polymer. C —Number of scissions per molecule of polymer. D_0 —Number of double bonds initially present per molecule of polymer.

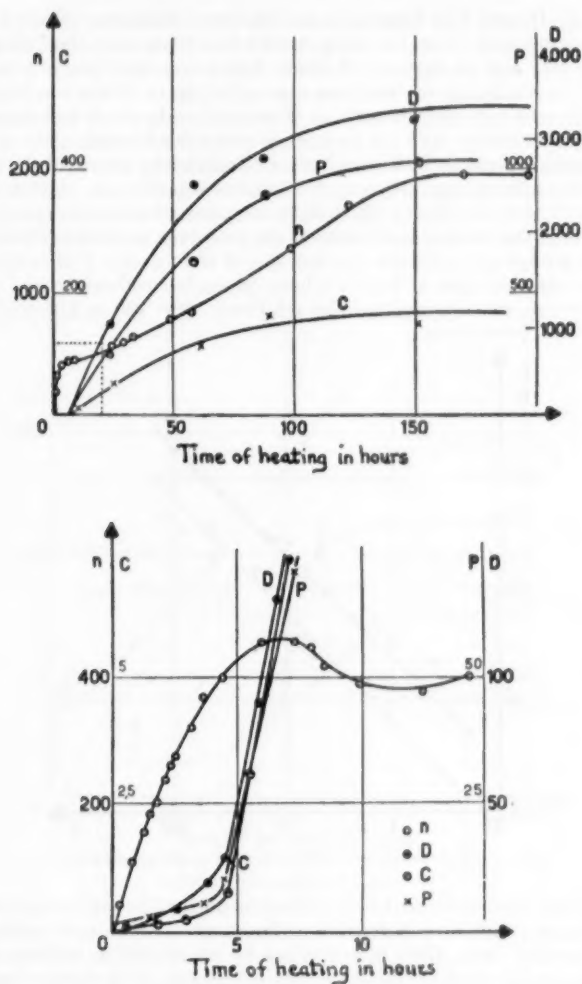


FIG. 3.—Degradation in the presence of an excess of oxygen at 110° C. *n*—Number of oxygen molecules absorbed per molecule of polymer. *C*—Number of scissions per molecule of polymer. *D*—Number of double bonds which are lost during the degradation, i.e., the difference between the number *D*₀ of double bonds originally present in the unheated polymer and the number of double bonds, determined at time *t*, in the same molecule. *P*—Number of peroxidic groups per molecule of polymer.

earlier observation has now been amplified and completed by a more thorough study of the relations between unsaturation, scissions, and peroxide formation. The method employed has been described earlier in this work.

The initial molecular weight of the fraction used was $265,000 \pm 5000$; the temperature of heating was $110^\circ \pm 0.5^\circ$ C. The experimental results are recorded in Figures 3a and 3b.

Curves *C*, *D*, and *P* in Figures 3a and 3b show analogies. During the first five hours of heating, they are merged with the time axis; then they ascend simultaneously, and at the end of about 150 hours they reach a horizontal plateau. The similarity of the three curves led us to determine the relation which might exist between the number of double bonds which had disappeared, the number of scissions, and the amount of peroxides formed.

The relations between *D*, *C*, and *P* were calculated by means of the curves in Figure 4, the ordinate and abscissa of which are logarithmic. Curve *D* shows the number *D* of double bonds which have disappeared per molecule of polymer as a function of the number *C* of scissions per molecule, and curve *P* the number of peroxide groups per molecule as a function of the number *C* of scissions.

The two straight lines of Figure 4 have an angle coefficient equal to unity. The ordinate at the origin gives the relations: $D = (20 \pm 2)C$ and $P = (6$

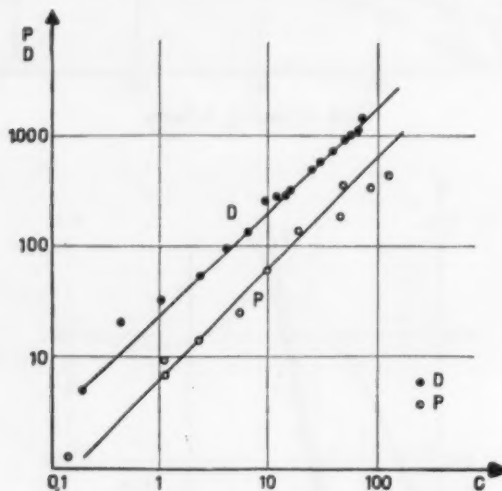


Fig. 4.—Relations between saturation, scission, and peroxidation.

$\pm 1)C$. These relations were found to be true during the entire duration of the degradation, i.e., they do not depend on the stage of progress of oxidation.

On a chemical basis, these relations can be interpreted as follows. During degradation in the presence of an excess of oxygen, if 20 double bonds of a molecule have been saturated, only one of these double bonds is the location of a scission reaction, and $6/2 = 3$ the location of peroxidation. This is, of course, based on the assumption that for each double bond there are two oxygen molecules in the peroxidic state, i.e., that there are two peroxidic groups. This conclusion explains the fact that the molecular weight of a degraded fraction is never lower than 15,000, which corresponds to a molecule of 20 elementary chain units of butadiene and 3 units of styrene.

It is noteworthy that the establishment of these relations between saturation, scission, and peroxidation is the key to the mechanism of degradation, and it is on this fact, which up to the present time had not been observed, that we have relied in establishing the scheme of the reactions (see Part II).

The degradation of GR-S in solution is accompanied by the absorption of oxygen (see Figures 3a and 3b, curve n). The course of the absorption curve does not make possible an expression of the phenomenon in the form of a simple equation. In order to analyze the reaction, the assumption was made that the total amount of oxygen consumed is the sum of the amounts consumed by each of the elementary reactions of oxidation.

In the present case (see Figure 5), the amount of oxygen consumed by the scission reactions and by peroxidation (curve B) were subtracted from the experimental absorption curve (see Figure 5). In the construction of this curve B, it was assumed that each peroxide contained one molecule of oxygen

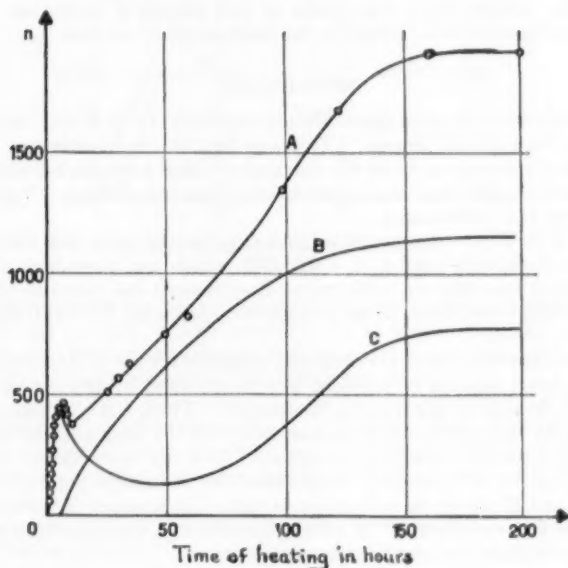


FIG. 5.—Absorption of oxygen.

and that one molecule of oxygen is required for each scission, in accord with the scheme: $\text{RCH}=\text{CHR}' + \text{O}_2 \rightarrow \text{RCHO} + \text{R}'\text{CHO}$.

The curve obtained by difference (C) represents the consumption of oxygen in the oxidation reactions, which involve neither scission nor peroxidation. A comparison of curves A and C makes it easier to interpret the oxygen consumption reaction. During the first 5 hours, A and C are practically indistinguishable. This is the *induction period* of degradation, in which there is an initial reaction between the solution and oxygen. It should be noted that, contrary to the scission, saturation, and peroxidation reactions, the oxygen consumption reaction does not manifest any induction period and begins as soon as heating is started. After this first 5 hours of heating, the curve C descends; part of the oxygen consumed during the induction period is consumed by scission and peroxidation reactions, while another part of the oxygen is desorbed, as indicated by the short descent of curve A. It is possible that the

initiation of degradation, i.e., the formation of the first scission products and the first peroxides, may involve a partial decomposition of the first absorption product, which then is a contributing factor in the amount of oxygen consumed during the period of cleavage (from 5 to 70 hours). At the end of 70 hours, curve C ascends progressively toward a plateau (750 moles of oxygen per polymer molecule), i.e., 1 oxygen molecule per 5 double bonds. There appears, therefore, between 70 and 150 hours, a new oxidation reaction, which can be attributed to the formation of alcohols, aldehydes, ketones, esters, epoxides, ethers, and acids, the presence of which has been detected in the oxidation products of polyisobutylenes²¹. Curve C during this final period is, in fact, similar to classic curves of the oxidation of hydrocarbons, aldehydes, and ketones²². No further study was made of this period of oxidation, since the present investigation was limited to the mechanism of scission.

PEROXIDATION

The peroxides present in the oxidation products of GR-S play an important part in the degradation process. To prove that this is so, one may study the appearance of scission reactions in a fraction of GR-S to which have been added natural peroxides obtained from a previously degraded solution. Figure 6 gives the results of this experiment.

Curve A in Figure 6 represents, as a function of time, the viscosity of a fraction, of molecular weight $M = 175,000$, which had been heated in a viscometer sealed from the air, while curve B represents the viscosity of the same fraction to which had been added a solution of degraded GR-S (1000 peroxidic groups per molecule).

The two curves A and B are distinctly separate for about 9 hours; then they join. The total number of scissions is not increased by the presence of peroxides, but the rate of degradation is changed. Thus, the viscosity is reduced to one-half its value in one and one-half hours for the pure solution and to 0.75 hour for the solution containing peroxides. This can be explained by the fact that the presence of peroxides suppresses the induction period of scission. Curves A' and B' show, as a function of time, the number of scissions taking place in the two solutions. The role of peroxides in this case is, therefore, to initiate the degradation and to induce scission.

Mesrobian and Tobolsky²³ attribute to benzoyl peroxide the role of an initiator of chain radicals, with formation of peroxides. However, this initiation takes place only if the peroxide concentration is very high. Nevertheless, the stable peroxides are, in reality, not alone responsible for the scissions. If a degradation process is interrupted during its progress, by removing gaseous oxygen, degradation stops immediately. This is illustrated by the following experiment.

A solution of GR-S was heated in air in a sealed ampoule for 2 hours at 140° C. Heating was then interrupted and the solution was divided into two ampoules. One was sealed in a vacuum, while the other was sealed in open air. After heating these for 48 hours at 140° C, the relative numbers of scissions and the relative amounts of peroxides in each portion were determined. The results are summarized in Table I.

In the absence of oxygen, degradation stops in spite of the presence of peroxides. The latter are decomposed, but their decomposition does not induce any new scissions. It should be recalled that the formation of stable peroxides takes place simultaneously with the saturation and scission reactions.

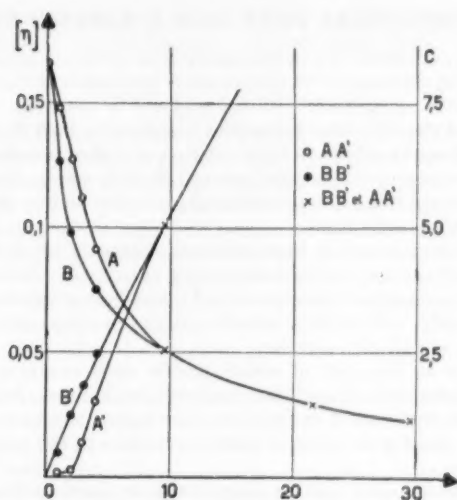
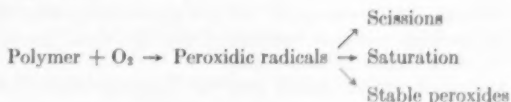


FIG. 6.—Natural and catalyzed degradation.

These phenomena can be explained if it is assumed that gaseous oxygen reacts with the polymer, with formation, not of stable peroxides, but of peroxidic radicals, which subsequently induce scission and saturation reactions, and part of which are converted with stable peroxides.

It was proved that phenyl-2-naphthylamine in solution (1 gram per 100 grams of polymer) inhibits degradation. This fact seems to confirm the preceding hypothesis if it is assumed that, as in the case of natural rubber, an anti-oxygenic agent can function as a deactivator toward any peroxidic radicals which may form²⁴.

The principal steps of the degradation can be represented diagrammatically by the following scheme:



The second part of this investigation will explain the complete mechanism of degradation, by oxidation, of GR-S in solution and will describe a kinetic study of this mechanism.

TABLE I

Time of heating at 140° C	Molecular weight	Scissions per molecule	Amount of peroxides per molecule
Initial state	180,000	0	0
2 hours in air	17,000	9	50
48 hours in vacuum	16,000	10	0
48 hours in air	1,250	140	900

II. THEORETICAL PART AND A KINETIC STUDY

The essential purpose of this investigation is to develop a scheme of reactions which is capable of explaining the phenomenon of scission of the GR-S molecule when air is made to act upon it with the polymer in solution.

In the light of the experimental results described in Part I of this work and of theories of different authors on the oxidation of olefins, we shall discuss what are the possible elementary reactions between the polymer molecule and oxygen with a view to establishing a mechanism of oxidation and to offer some proofs of its validity on a kinetic basis.

The scission reaction can be included on the category of oxidation reactions by the fact that it occurs only in the presence of oxygen. However, it cannot be studied independently of saturation and peroxidation reactions, which proceed simultaneously. In reality, scission always accompanies the process of the autoxidation of GR-S in solution.

GR-S belongs in the class of olefins insofar as it contains double bonds. However, the mechanism of oxidation proposed by Farmer, Bolland, Gee, and their collaborators²⁵ does not explain the cleavage of the molecules, although Farmer has reported the presence of scission products in the oxidation products of natural rubber.

There are, nevertheless, certain phenomena common to the mechanism of the degradation of GR-S and the mechanism of the oxidation of olefins.

(1) The two processes are chain reactions which propagate through the intermediary action of free radicals. Numerous studies of the oxidation of hydrocarbons²⁶ have established the fact that the reaction between gaseous oxygen and hydrocarbons in the liquid phase is a chain reaction. In the case of GR-S in solution, we have been able to prove that the scission reaction does not show the characteristics of a reaction of the side chains, and the exponential law of the rate Ae^{kt} has not been verified, and the induction period could be interpreted as the time necessary to establish the stationary state. After this induction period, the first-order law with respect to the double bonds is found to hold true. Moreover, since the influence of the temperature on the rate of the reaction conforms to the law of Arrhenius, it might seem reasonable to interpret the phenomenon by a mechanism involving the reaction of straight chains, with establishment of a stationary state. Let it be noted, however, that certain side chains termed "degenerated" do not appreciably alter the characteristics of a straight-chain reaction because of the fact that the contribution of radicals from the side chains is very small.

(2) Both the oxidation of olefins and the degradation of GR-S are characterized by the formation of peroxides. However, the mechanism of this peroxide formation seems to be very different in the two cases.

Farmer has proved that, in the first stages of the oxidation of polyisoprenes, all of the oxygen combines in the hydroperoxidic state, without any accompanying change of the degree of saturation. It is the hydroperoxide which initiates the oxidation. In the case of hydrocarbons carefully freed of peroxides, George and his collaborators²⁷ have come to the conclusion that, previous to the formation of any peroxides, intermediate activated products capable of reacting with oxygen must be formed. The chain then propagates itself by thermally activated molecules and not by free radicals.

GR-S seems to be an intermediate case. At the beginning of oxidation, the oxygen which is consumed is not in the form of peroxides, and these do not appear until the unsaturation decreases.

The comparison of the behavior of different olefins gives the opportunity to establish definitely the mechanism of oxidation of GR-S.

PROGRESS OF DEGRADATION

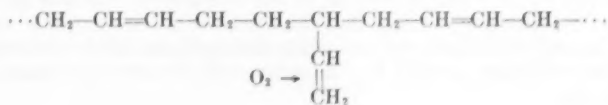
It has already been established that when GR-S in solution is exposed to the attack of atmospheric oxygen (see Part I), there is an induction period, which lasts 4-5 hours at 110° C. During this time, oxygen is consumed (450 moles of oxygen per polymer molecule of molecular weight $M_0 = 260,000$), without any change of the degree of saturation, nor any scission reaction, nor any formation of stable peroxides which can be detected by the method of Bolland. This consumption of oxygen is a zero-order reaction, as indicated by the fact that the amount of oxygen absorbed during the first 5 hours is proportional to the time of heating (see Part I, Figure 3). We have established experimentally that this reaction proceeds with an activation energy of 11 ± 2 kcal.

The fact that the unsaturation remains unchanged during this period makes this zero-order reaction open to consideration as a phenomenon involving adsorption of oxygen by the solution, with formation of a complex. This interpretation has been suggested by earlier investigations of polymerization²⁸. For example, in order to explain the fact that the presence of oxygen has, on polymerization, the double effect of prolonging the time of the induction period and of increasing the rate of polymerization after this period and of increasing the rate of polymerization after this period, Melville and Pratt²⁹ assumed that a monomer-oxygen complex must be formed initially, the slow decomposition of which gives rise to a product capable of catalyzing the polymerization. The slowness of the start of polymerization would, then, be the result, not of an inhibition, but of an induction period in which free radicals are formed. This would explain why the rate of the reaction after the induction period is greater than the rate of polymerization without induction. It has been seen that the addition of peroxides suppresses the induction period. The complex should, consequently, not be itself a peroxide, but might be capable of producing peroxides.

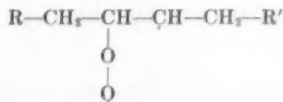
It is evident that we are not yet in a position to identify the nature of the complex. However, the low activation energy (11 kcal.) and the zero-order reaction suggest that this complex may be an adsorption product susceptible to decomposition, with formation of gaseous oxygen. We have proved, in fact, a slight desorption of oxygen at the end of this period. The role of this complex can, therefore, be regarded as that of an "oxygen supplier", which would promote all the oxidation reactions in the solution.

The fact that no peroxides are formed during the early stages of the degradation of GR-S is in contradistinction to the experiments of Farmer and Sutton³⁰ with polyisoprenes of low molecular weights, specifically dihydromyrcene, dihydrofarnesene, and squalene, in which case the initial oxidation product is a hydroperoxide, the formation of which does not change the degree of saturation.

The presence of side-chain double bonds in GR-S might lead to the belief that oxygen reacts preferentially at these double bonds:



Finally, the evaluation of the heats of reactions can serve only to establish whether a reaction is thermodynamically possible, but not whether it can take place kinetically, for this latter possibility depends on the activation energies. It seems reasonable to conclude that, in the case of GR-S, the attack by oxygen can take place at the double bond rather than at the α -methylenic carbon atom, as in the chlorination of rubber³⁵. The first radical formed would, then, be of the type:

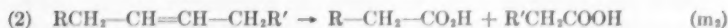
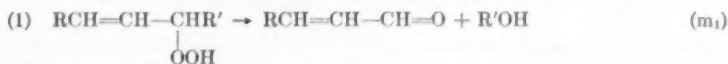


NATURE OF THE INTERMEDIATE RADICALS

Current theories of scission reactions call for the active role of free radicals of the types: hydrocarbon radicals R^* and peroxide radicals ROO^* . The majority of reactions involving the oxidation of hydrocarbons start by detachment of a mobile hydrogen atom. The first radical formed is a hydrocarbon radical, which can combine at the oxygen atom, with formation of a peroxide radical. The latter then reacts with the hydrocarbon, with formation of a new hydrocarbon radical³⁶.

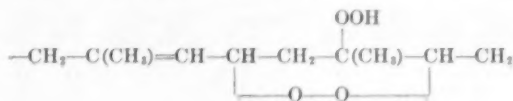
Although this mechanism is true of the oxidation of polyisoprenes³⁶, it does not explain the formation of scission products. Farmer³⁷ has called attention to the fact that scissions occur easily and in considerable amount at the γ - δ double bond of ethyl sorbate and at the α - β double bond of diphenylbutadiene, as well as at the double bonds of polyisoprenes³¹. Farmer concluded that there is an addition reaction of oxygen at the double bond, with formation of peroxide, cyclization and, finally scission.

A more recent work of Mitchell and Shelton³⁸ on the oxidation of 5-phenyl-2-pentene indicates the possibility of GR-S undergoing two scission reactions:



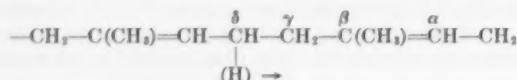
It should be noted that the experimental results of Mitchell and Shelton³⁸ are in accord with those of the present investigation. They prove, in fact, as does the present work, that the decrease of unsaturation takes place simultaneously, with the formation of oxidation products. This, in the opinion of the present author, makes reaction m_1 a doubtful one. The analyses of Mitchell and Shelton of the scission products show that ketones and aldehydes are first formed and that these are then oxidized to acids and esters.

Bolland and ten Have³⁹ have shown that, at the commencement of the oxidation of polyisoprenes, oxygen combines in groups of four atoms. This makes probable the formation of a biperoxide of the type:

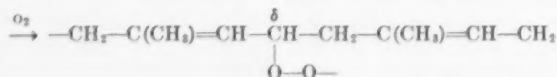


This peroxide may be formed in the following way:

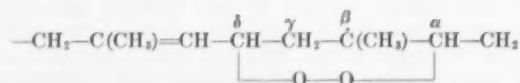
- (1) Attack of the δ -carbon atom, with formation of a hydrocarbon radical:



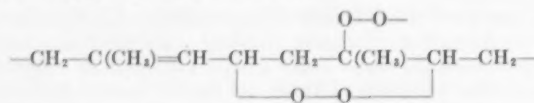
- (2) Addition of oxygen at the δ -carbon atom, with formation of a peroxide radical:



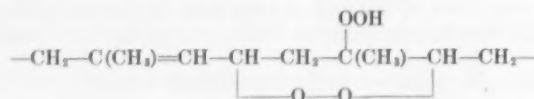
- (3) Opening of the double bond and cyclization between the α - and δ -carbon atoms:



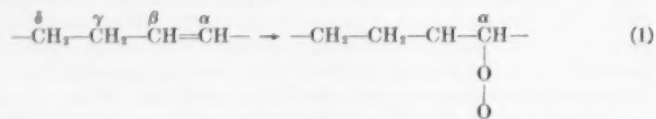
- (4) Addition of oxygen to the β -carbon atom:



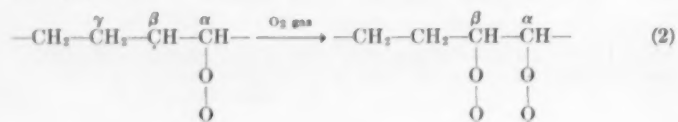
- (5) Combination of the hydrogen atom detached by reaction (1) with the β -peroxide radical, with formation of a hydroperoxide:



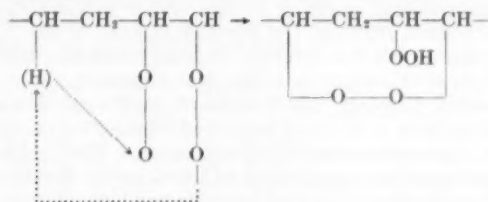
This mechanism, involving five steps, and accepted by Bolland and Farmer, is based on the hypothesis that the first point of attack of the molecule is the δ -carbon atom. If, on the other hand, it is assumed that, in the case of GR-S, opening of the double bond takes place preferentially to the substitution reaction, then the first radical to be formed would be:



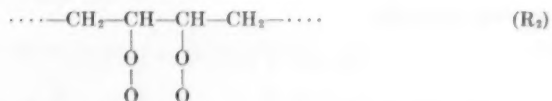
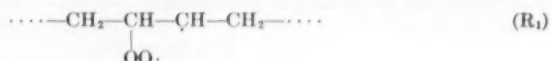
and this reaction would be followed immediately by the addition of one oxygen molecule at the β -position:



and by attack on the δ -CH₂ group by the α -COO group, with cyclization and migration of hydrogen:



In this the final product would be the same type of peroxide, but the sequence of the reactions would be the reverse of that proposed by Bolland. If this process is envisioned for GR-S, two types of peroxidic radicals can be conceived:



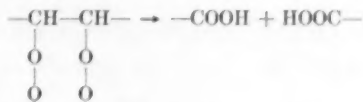
The first radical R₁ should be capable of combining with gaseous oxygen, with formation of either R₂ or the stable biperioxide P.



The only radicals taking part would be peroxidic radicals, with the exclusion of hydrocarbon radicals.

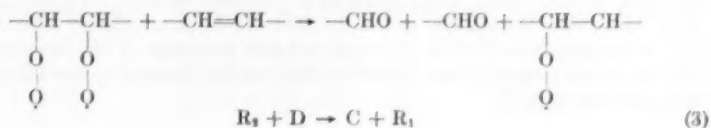
SCISSION REACTIONS

On the basis of the foregoing, the biperoxidic radicals R₂ are, in the opinion of the present author, responsible for scission. At first thought, a monomolecular reaction might be imagined:



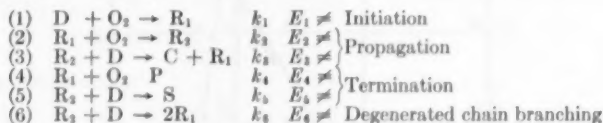
with formation of an acid. In reality, the majority of the scission products are neutral¹⁰, i.e., aldehydes or ketones, which are subsequently oxidized in part to acids.

Interreaction between the R₂ radical and another double bond D could bring about a scission C, leading to aldehydes, with transfer of a part of the reactivity to a new R₁ radical, according to the following scheme:



REACTION KINETICS

A kinetic study of the group of reactions which has just been proposed makes it possible to determine to just what an extent this mechanism is valid. Consider the following six successive reactions:



k_i and $E_i \neq$ represent the rate constants and the activation energies of each of the reactions. The concentrations of each of the components D , O_2 , R_1 , R_2 , C , and P are represented by the same symbols in parentheses: (D) , (O_2) , (R_1) , (R_2) , (C) , and (P) . Assuming the stationary state for the R_1 and R_2 radicals, the rates of the reactions can be represented by the following expressions.

Rate of the scission reactions:

$$dC/dt = \frac{k_1 k_2 k_3 (O_2) (D)}{k_2 (k_5 - k_6) + k_4 (k_3 + k_5 + k_6)} \quad (a)$$

It may be assumed that, in the presence of an excess of oxygen, (O_2) constant. Hence:

$$dC/(dt) = K_s(D)$$

The rate of saturation, i.e., the rate of disappearance of double bonds, can be expressed, on the basis of the proposed mechanism, by the relation:

$$-dD/dt = k_1(D)(O_2) \left[1 + \frac{k_2(k_3 + k_5 + k_6)}{k_2(k_5 - k_6) + k_4(k_3 + k_5 + k_6)} \right]$$

$$-dD/dt = K_d(D) \quad (b)$$

and the rate of peroxidation, i.e., the rate of formation of stable peroxides, can be expressed thus:

$$dP/dt = k_4(R_1)(O_2) = \frac{k_1 k_4 (k_3 + k_5 + k_6) (D) (O_2)}{k_2 (k_5 - k_6) + k_4 (k_3 + k_5 + k_6)}$$

$$+ dP/dt = K_p(D) \quad (c)$$

In accord with the scheme of the reactions which are proposed, the scission, saturation, and peroxidation reactions are of the first order with respect to the double bonds. This has been verified experimentally by studying the changes of these rates as a function of the concentration D of double bonds. It can be shown, as in Figure 7 for a fraction of initial molecular weight $M_0 = 100,000$, and heated at 100°C , that the curves are straight lines after the induction period. This proves that the three reactions are of the first order with respect to the double bonds. From this fact the following three relations are derived:

$$-dD/dt = 8.2 \times 10^{-2} (D) \quad (b')$$

$$dC/dt = 0.4 \times 10^{-2} (D) \quad (a')$$

$$dP/dt = 2.3 \times 10^{-2} (D) \quad (c')$$

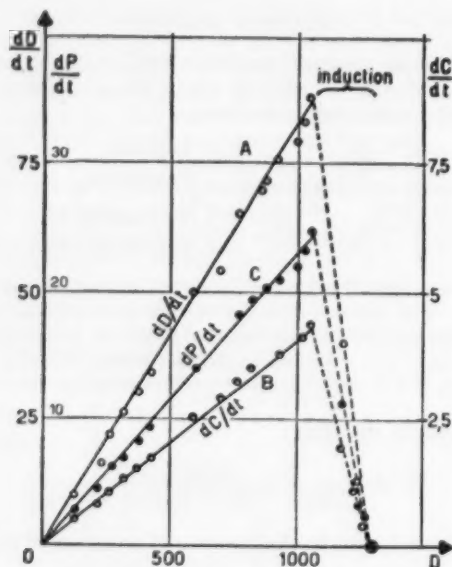


Fig. 7.—Changes of the rate, $-dD/dt$, of the saturation reaction, of the rate, dC/dt , of the scission reaction, and of the rate, dP/dt , of the peroxidation reaction, as functions of the number D of double bonds present at time t in one polymer molecule of $M_s = 100,000$. The rates are expressed in the following units: dD/dt = number of double bonds lost by one polymer molecule by heating 1 hour at 110°C . dC/dt = number of ruptures occurring in one polymer molecule by heating 1 hour at 110°C . dP/dt = number of peroxidic groups, —O—O— , which appear in one polymer molecule by heating 1 hour at 110°C .

At the beginning of the reaction, when D is in the range of 1050 to 1300 (induction period), the first-order law does not hold true. Furthermore, it is probable that the stationary state is not established during this period and that the expressions for the rates (a), (b), and (c) shown above are not applicable.

INFLUENCE OF THE TEMPERATURE

A change of temperature changes the ratio of the number of peroxidic groups to the number of scissions per polymer molecule. It was found experimentally that the proportion of the number P of peroxidic groups which are formed to the number C of scissions is as follows:

Temperature	P/C ratio
80°C	4 ± 1
110°C	6 ± 1
140°C	10 ± 1

A rise of temperature therefore favors the formation of peroxides, the activation energy E_P of which is greater than the activation energy E_C of the scission reaction. The difference between E_P and E_C can be calculated by the Arrhenius law:

$$K_P = A_P \cdot e^{-E_P/RT}$$

$$K_C = A_C \cdot e^{-E_C/RT}$$

where K_P and K_C are the rate constants of the peroxidation reaction and scission reaction, respectively, A_P and A_C are factors which are independent of temperature, R is the gas constant ($R = 1.98$), and T is the absolute temperature.

Since the reactions are of the first order, the relation of the rates is:

$$\frac{dP/dt}{dC/dt} = \frac{A_P}{A_C} \cdot e^{-E_P + E_C/RT}$$

or, in logarithmic form:

$$-E_P + E_C = RT \log_{10} \alpha + RT \log_{10} \frac{A_C}{A_P}$$

Applying this to the experimental curves, we obtain:

$$\begin{aligned} -E_P + E_C &= -5(\pm 1) \text{ kcal. per mole} \\ A_P/A_C &= 3(\pm 1) \times 10^{-4} \end{aligned}$$

The value of $-E_P + E_C$ thus derived agrees with the direct determinations of E_P and E_C .

The activation energies of the scission and peroxidation reactions were derived from a study of the influence of temperature on their rates⁴⁴.

$$\begin{aligned} E_C &= 19 (\pm 0.2) \text{ kcal. per mole} \\ E_P &= 25.5 (\pm 0.5) \text{ kcal. per mole} \end{aligned}$$

whence

$$-E_P + E_C = 6.5 (\pm 0.7) \text{ kcal. per mole}$$

This value for $-E_P + E_C$ agrees satisfactorily with the preceding result.

ACTIVATION ENERGIES OF THE OXYGEN ABSORPTION REACTIONS

During the degradation of GR-S, oxygen is consumed in an irregular fashion, and three periods are distinguishable, viz., an induction period, a period of cleavage, and a final period. The present study of the rate of consumption at different temperatures shows that there is an activation energy characteristic of each period. Thus, the energy for the induction period is $11 (\pm 2)$ kcal. per mole, the energy for the rupture period is $16 (\pm 0.2)$ kcal. per mole, and the energy for the final period is $27.2 (\pm 0.2)$ kcal. per mol.

The value of the activation energy of the oxidation of GR-S in solution (rupture period) is close to that which Bolland calculated for the photooxidation of dihydromyrcene (diisoprene), viz., $E_r = 17$ kcal. per mole. The mechanism of the chain reaction depends on the relative values of the rates of the propagation and short-stop reactions.

In the case of GR-S, reaction (2) supplies the R_2 radicals, which are utilized by reactions (3), (5), and (6). This reaction (2) proceeds in competition with reaction (4), which gives the stable peroxide. In order for the chain to be able to propagate, the rate constant of reaction (2) must be greater than the rate constant of reaction (4).

The relation between K_2 and K_4 can be determined from the experimental values of the rates at 110°C (see Equations (a), (b), (c), (a'), (b'), and (c') above). If it is assumed that k_3 is very large in comparison with $k_5 - k_6$, there is finally derived:

$$\frac{k_4}{k_2} = 0.39$$

The value of k_2 is, therefore, approximately three times as great as that of k_4 . That k_2 is greater than k_4 is confirmed by the relation between the activation energies E_2 and E_4 .

This relation is derived from Equations (a), (b), and (c) and from the following equation:

$$-dO_2/dt = \frac{k_1[1 + (k_2 + k_4)(k_3 + k_5 + k_6)(D)(O_2)]}{k_2(k_5 - k_6) + k_4(k_3 + k_5 + k_6)}$$

If it is assumed that the k_1 constant is small in comparison with the product: $k_1(k_2 + k_4)(k_3 + k_5 + k_6)$, the relation of the rates become, after simplification:

$$\frac{dP/dt}{-dO_2/dt} = \frac{k_4}{k_3 + k_4} \approx \frac{k_4}{k_2}$$

If E_P and E_{O_2} represent the experimental activation energies of the peroxidation reaction and oxidation reaction, respectively, then:

$$E_P - E_{O_2} = E_4 - E_2 = 26 \text{ kc} - 16 \text{ kc} = 10 \text{ kc}$$

Reaction (4), involving the formation of stable peroxides, has, therefore, an activation energy which is higher than the activation energy of formation of R_2 radicals. This greater energy makes possible propagation of the chain.

CONCLUSIONS

The investigation which is described in the present paper brings to the problem of aging some new facts which throw light on the phenomenon of scission.

From the experimental point of view, the work renders available a new experimental technique, by means of which it is possible to make simultaneous determinations of oxygen, double bonds, peroxides, and scissions.

The experimental results demonstrate the existence of a close relation between the changes of the degree of saturation, number of scissions, and formation of peroxides. The fact that gaseous oxygen is indispensable to the reaction involving cleavage of the polymer molecules has led the present author to assume the existence of a new "biperoxidic" radical, the presence of which in the system explains unequivocally the complex role which the peroxides play.

It should be noted that the majority of investigations previously published have made use of small molecules which could serve as models, whereas the study described in the present paper is based on the opposite technique, in which the study of macromolecules is, to draw an analogy, a "microscopic" study. Thus, the scission reaction is a very sensitive test for high polymers, whereas chemical analysis of the scission products of small molecules presents difficulties which are at times insurmountable. It is this magnified approach in the present investigation which, indirectly, has made it possible to prove that addition reactions at the double bonds predominate and take place preferentially to substitution reactions at the CH_2 group. There seems, then, to be a relation between the structure of olefins and the point of attack by oxygen. It may be that, in certain cases, the addition and substitution reactions proceed simultaneously. In this case there would be superposition of several mechanisms.

The present investigation does not pretend to offer a complete mechanism of the oxidation of GR-S, but only describes a series of reactions which are in accord with the experimental results obtained in the study of scission reactions.

SUMMARY

The mechanism of the scission reactions in the oxidation of GR-S in solution is explained on the basis of a series of bimolecular reactions.

The initial point of attack on the polymer by oxygen takes place at the double bond, with formation of a peroxidic radical, $R-CH=CH-R' \rightarrow R-CH(OO)\cdot-CH-R'$. This latter, in turn, adds a molecule of oxygen, with formation of a biperoxidic radical, $R-CH(OO)\cdot-CH(OO)\cdot-R'$. This new radical is very active, and is in reality the only agent responsible for the saturation and scission reactions, which it sets in motion by its attack on other double bonds.

The determination of the activation energies and of the orders of the scission, saturation, and peroxidation reactions confirms this mechanism.

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INFRARED STUDY OF THE OXIDATION OF ELASTOMERS *

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INTRODUCTION

Until relatively recently, little was definitely known concerning the chemical changes involved in the oxidation of natural or synthetic rubbers. However, chemical researches made on the oxidation of hydrocarbons by a number of investigators¹, particularly by Farmer and his coworkers², have provided a considerable amount of information concerning such reactions which might be typical of rubberlike materials. As a result of these studies, it is generally concluded that, in the initial stage of the oxidation reaction, practically all of the oxygen absorbed by the hydrocarbon sample is utilized in the formation of hydroperoxides. The secondary reactions which these hydroperoxides undergo form products of oxygen-containing groups which can be and probably are highly complex.

In order to ascertain the nature and relative proportion of the functional groups contained in the products of the oxidation reaction, Hilton³ and Naylor⁴ made a study of the distribution of oxygen in a highly oxidized rubber. Hilton reported that only about 60 per cent of the oxygen in a rubber sample containing about 11 per cent combined oxygen could be accounted for by chemical methods of analysis. The 40 per cent of the combined oxygen unaccounted for is deduced to be present in the form of ether or peroxide groups, for which no direct method of estimation is known. Of the 60 per cent combined oxygen which has been identified with definite functional groups, about one-half appears in the form of hydroxyl groups. The other half appears as mostly or all carbonyl, carboxyl, and ester groups. Since these functional groups are the products of over half of the oxygen utilized in the total reaction, the infrared spectrum should be a useful medium for identifying these structural groups and possibly provide a clue for identifying structures resulting from the reactions of the unaccounted for portion of oxygen.

Accordingly, an exploratory investigation has been started, in which an attempt has been made to follow the oxidation reaction products by the application of infrared methods. Structural changes resulting from oxidation have been compared for several elastomers. Observations have been made on the structural changes as they are affected by antioxidants, temperature, the presence of trace amounts of iron, and ultraviolet radiation. Information has been obtained concerning the amount of oxygen required to cause such functional groups as hydroxyls and carbonyls to become evident in the absorption spectrum. Since oxidation affects the physical properties of these materials, an attempt has been made in a few limited cases to correlate the appearance of characteristic absorption bands with stress-strain data.

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EXPERIMENTAL PROCEDURES

Among the polymers investigated were several types of polyisoprenes and polybutadienes, Neoprene and butadiene-styrene copolymers. In most cases, the polymers were purified by dissolving in benzene and precipitating in acetone, which was repeated three times to remove impurities, particularly antioxidants. The purified samples were dried in a vacuum oven. The purified polymers were then put in solution in benzene, shielded from the light, and stored at 0° C in a nitrogen atmosphere. Precautions were taken in handling to minimize exposure to light and air. Where studies were made with chemical additives, these were placed in benzene solution and added to the purified polymer solution in the proper amounts.

The film samples used for infrared analysis were prepared from benzene solutions having approximately 2 per cent polymer concentration. The solvent was evaporated from a measured volume of solution placed in a small, flat, steel frame placed on a glass plate covered with plain, transparent cellophane. After completion of solvent evaporation, the polymer film was removed from the cellophane by soaking briefly in water. The films prepared in this manner were approximately 0.02 mm. thick. The infrared spectra were recorded by means of a conventional double-beam spectrometer, with rock salt optics.

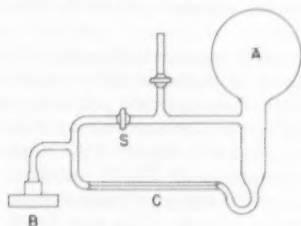


Fig. 1.—Device for oxygen absorption measurements.

The device for measuring oxygen absorption is shown schematically in Figure 1. It consists of a relatively large volume A (about 500 cc.), which is connected to a small absorption cell (about 10 cc.) by means of a capillary tube, C. A second connection between these two volumes is through a stopcock, S. A small reservoir contains a low vapor-pressure liquid, maintained at a level which will not flow across the capillary except by pressure differences existing between the two volumes. As the polymer sample absorbs oxygen, the liquid moves across the capillary. The distance of travel is a measure of the volume absorbed. When the liquid reaches its useful limit of movement, it can be reset by opening the stopcock, S.

The absorption cell is made of stainless steel and is connected to the system through a ground glass-stainless steel tapered joint. The cell is constructed in two pieces so that the polymer films, on their stainless steel frames, can be introduced. Vacuum tight seals are made by mercury pools at the interfaces of the cell assembly and tapered joint. The entire system is kept in a thermostat maintained at 40° ($\pm 0.5^\circ$) C.

OXIDATION OF PURIFIED ELASTOMERIC MATERIALS

In studying the mechanism of oxidation in the synthetic rubber polymers, one might expect to find a similarity in the structures of the products of oxidiz-

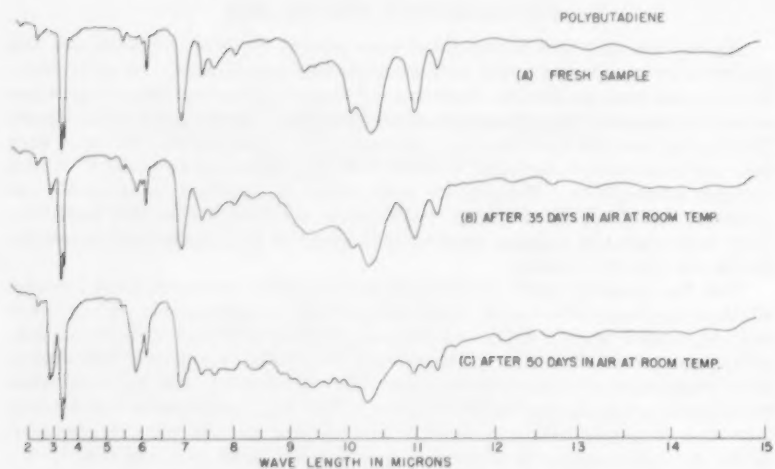


FIG. 2.—Infrared spectra, showing progressive oxidation of a purified emulsion polybutadiene.

ing reactions occurring in these polymers, since the information available from low-molecular olefins indicate such reactions to be similar.

The absorption spectrum of an emulsion polybutadiene is shown in Figure 2. The antioxidant and other impurities were removed by the method previously described. The spectrum, shown in Figure 2(A), represents the characteristic absorption bands from a freshly made film of polymer. The spectrum, shown in Figure 2(B), was taken of the same polymer sample after 35 days' exposure to light and air at room temperature. The new bands appearing at 3 and 5.8

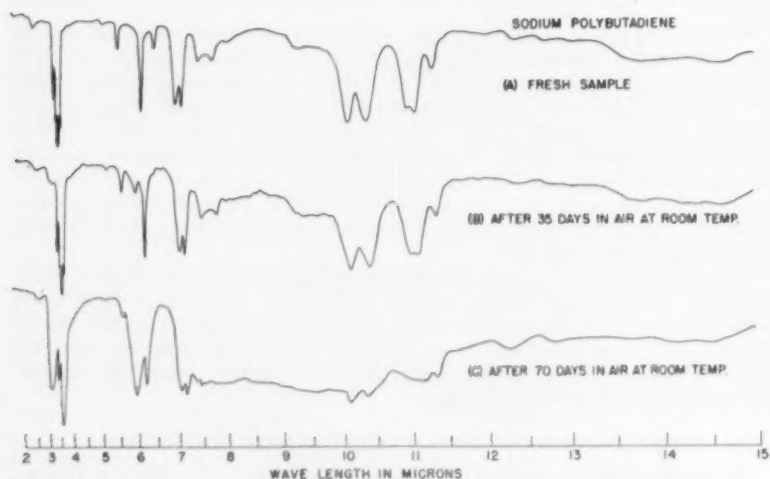


FIG. 3.—Infrared spectra, showing progressive oxidation of a purified sodium polybutadiene.

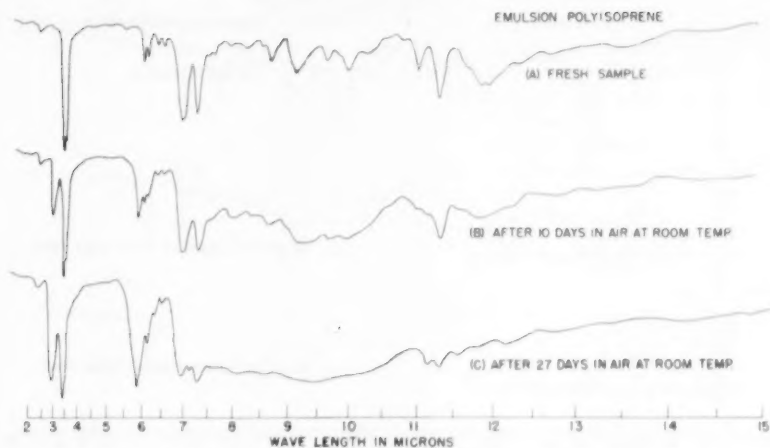


FIG. 4.—Infrared spectra showing progressive oxidation of a purified emulsion polyisoprene.

microns result from the vibration frequencies of the hydroxyl and carbonyl structures. There is no appreciable change of the intensity of the carbon double bond absorption band. The increased absorption and broadening of the 9.3 micron band suggests the formation of complex carbon and oxygen structures which would be expected to appear in this region of the spectrum. The spectrum of this sample after 50 days' exposure to light and air at room temperature is shown in Figure 2(C). The absorption of the hydroxyl and carbonyl structures is considerably stronger. However, the carbon double-

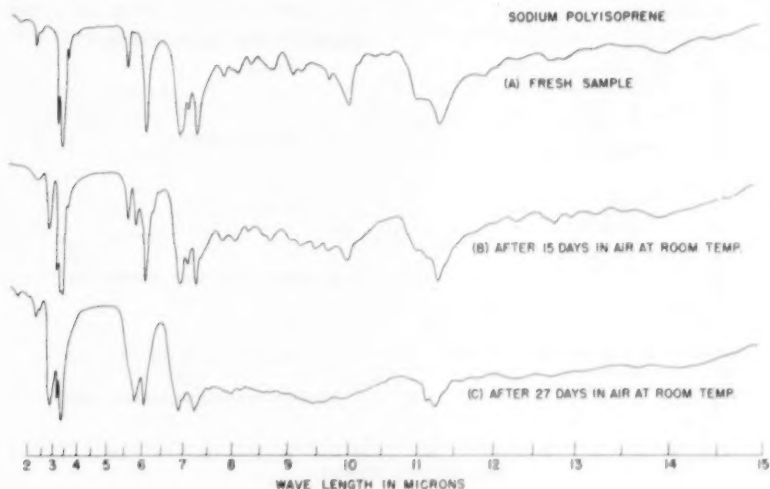


FIG. 5.—Infrared spectra, showing progressive oxidation of a purified sodium polyisoprene.

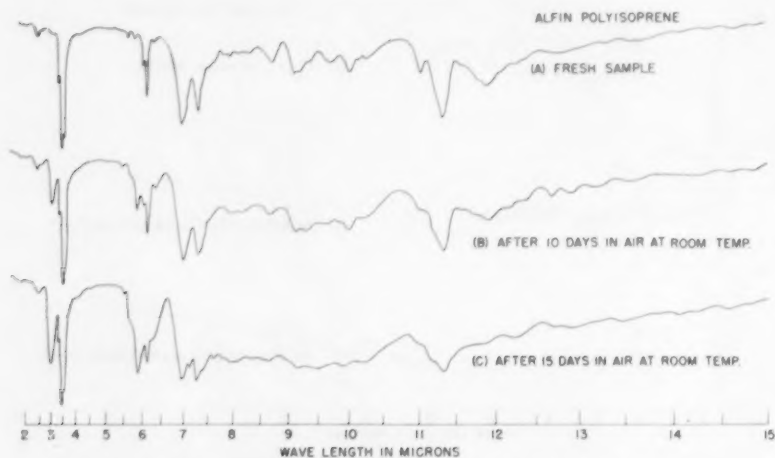


FIG. 6.—Infrared spectra, showing progressive oxidation of a purified alfin polyisoprene.

bond band is not appreciably reduced in its intensity, although it is strongly overlapped by the intense carbonyl band. This suggests relatively little change of the unsaturation of the polymer. A strong general absorption now masks out the absorption bands appearing in the 7 to 11 micron range of the spectrum.

The changes in the absorption spectrum of a sodium catalyzed polybutadiene brought about by oxidation is shown in Figure 3. The characteristic spectrum of a fresh sample is shown in Figure 3(A). The same sample was

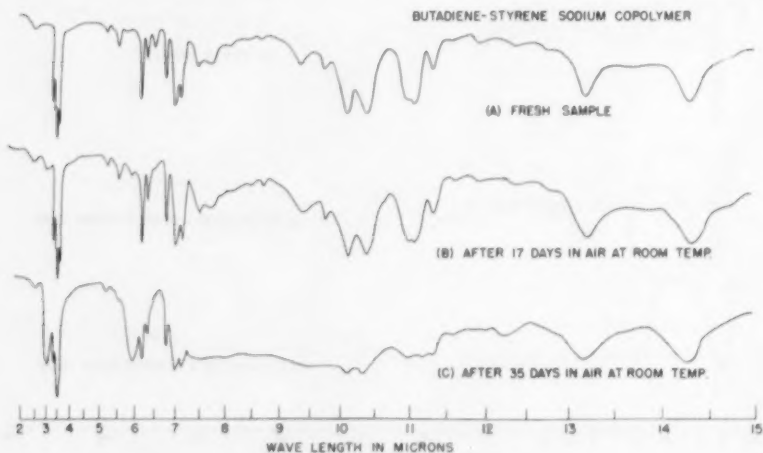


FIG. 7.—Infrared spectra, showing progressive oxidation of a purified butadiene-styrene sodium copolymer.

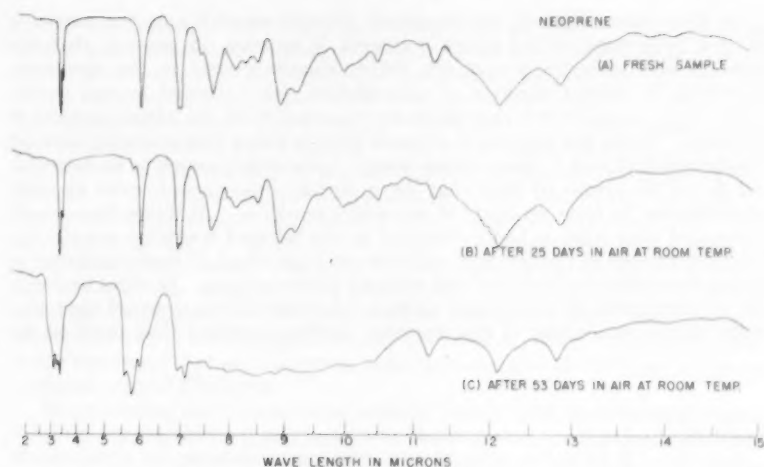


FIG. 8.—Infrared spectra, showing progressive oxidation of a purified Neoprene.

examined after the oxidation reaction had proceeded for 35 and 70 days. The spectral changes are shown, respectively, in Figures 3(B) and 3(C).

The spectra of oxidized and unoxidized elastomers are shown in Figures 4 through 9. These include the following; emulsion polyisoprene, sodium-catalyzed polyisoprene, and alfin polyisoprene, sodium-catalyzed butadiene-styrene copolymer, Neoprene, and Butyl rubber. With the exception of Butyl rubber, the same characteristic changes appear in the spectrum on oxidation. In the case of Butyl rubber, it is presumed that the oxidation rate is much less than in the other materials, due to the low amount of unsaturation. In this case, one would not expect to observe any great changes in the spectrum.

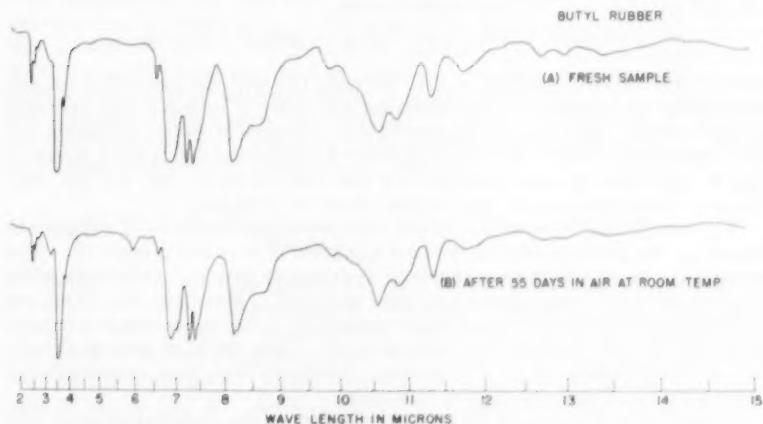


FIG. 9.—Infrared spectra, showing progressive oxidation of a purified Butyl rubber.

In the observations of the structural changes occurring as the oxidizing reaction progressed in the above polymers, it appears, in general, that the hydroxyl and carbonyl groups are visible simultaneously in the spectrum. According to current theories of autoxidation, the hydroxyl groups should appear first, since the hydroperoxides are supposed to be the initial products of oxidation. From the analysis of infrared data, it seems very probable that the concentration of such hydroperoxide groups is not great enough to be detected, and it can be presumed that they have already decomposed, even at room temperatures, to form products of secondary reactions. If this is the case, it is assumed that what is being observed in the infrared spectrum are the hydroxyl structures in the terminal reaction products which Hilton³ concluded as arising from alcoholic hydroxyl and enolized ketone groups. In order to clarify the interpretations of the infrared spectra, it became necessary to get some idea of the minimum amount of the observed functional groups that could be de-

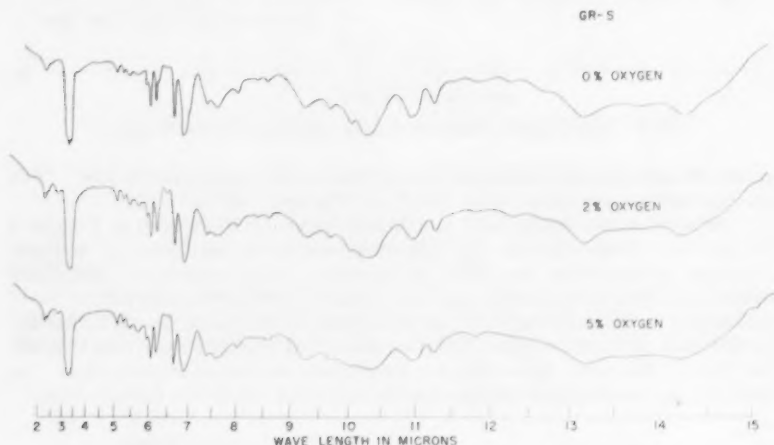


Fig. 10.—Relationship between spectral change and amounts of oxygen absorbed.

tected in the infrared spectrum and to correlate this with the amount of oxygen absorbed by the polymer. The minimum quantities of hydroxyl and carbonyl groups were determined by mixing appropriate amounts of octadecyl alcohol and ethyl stearate in GR-S. It was determined from the spectra of these mixtures that a minimum of approximately 0.5 per cent hydroxyl and 0.1 per cent carbonyl concentrations on the polymer could be detected.

The correlation between the direct volumetric measurement of oxygen absorbed by the polymer and its infrared spectrum is shown in Figure 10. The spectrum shows no definite evidence of hydroxyl or carbonyl structures when as much as 5 per cent oxygen has been absorbed. However, the 10-micron region of the spectrum shows a general absorption in this range, which increases progressively with increase in oxygen content. This region of general absorption is characteristic of all the oxidized polymers that were examined (see Figures 2-9) and deserves further discussion.

According to the data of Hilton³, cited earlier on the distribution of oxygen in highly oxidized rubber, it was deduced that 40 per cent of the combined

oxygen was present in the form of peroxide or ether groups. Naylor⁴ concluded that it was reasonable to expect epoxides to be present in oxidized rubber. If these functional groups are included in the products of polymer oxidation, one should expect to find evidence of their presence in the 8- to 12-micron range of the infrared spectrum. The spectra of a number of reference compounds including these structures are available. Shreve and coworkers⁵ have made some correlations of hydroperoxides, peroxides, and epoxides, and their parent compounds. They concluded that hydroperoxide groups give rise to characteristic absorption bands near 12 microns and that linkages are responsible for strong absorptions in the 10- to 12-micron range. However, they found that this latter band is very sensitive to the structures attached to the peroxide linkage and will shift accordingly. They also found that the spectra of oxirane derivatives of long chain olefins show bands of medium intensity near 7, 8, and 9 microns, as well as two strong bands near 11 and 12 microns. In another study⁶, it was concluded that an absorption band characteristic of the epoxy structures appeared around 8 microns.

In correlating the spectral data, outlined above, with the absorption curves obtained for the oxidized polymers, one observes that the characteristic bands attributed to the peroxide groups at 11 and 12 microns fall outside the range of general absorption, and are not evident in these spectra. Empirical spectral data indicate, however, that both alcohols and ethers are strong absorbers in this spectral region of interest. This is unfortunate, because it becomes impossible to distinguish one from the other of these functional groups by infrared methods. It has been established by Hilton³ that about one-fourth of the oxygen absorbed in highly oxidized rubber is accounted for in the form of alcohols. The presence of an alcohol is confirmed by the strong absorption band at 3 microns. The onset of general absorption in the 10-micron region of the spectrum before the appearance of the hydroxyl bands at 3 microns, and the absence of bands at 11 and 12 microns due to peroxides, leads to the conclusion that the major portion of the 40 per cent unaccounted for oxygen must be involved in a complex assortment of ether linkages. This is essentially in agreement with the data of Naylor⁴, who proposes that ethers and esters result from subsequent reactions with alcohol groups, therefore reducing the concentration of the latter in the early stages of the secondary oxidation reactions. The probability that epoxy groups are present in any appreciable amount is ruled out on the basis that such structures result from reactions involving the double bond⁴ and a relatively small reduction of unsaturation is observed in the spectrum. Obviously, the appearance of the carbonyl band near 5.8 microns in the spectra of all the oxidized samples indicates the presence of ester and ketone structures in the oxidized products.

EFFECT OF TEMPERATURE AND OTHER VARIABLES ON THE OXIDATION OF GR-S

Infrared methods were applied to follow the structural changes produced by oxidation of GR-S under a variety of conditions. The effect of temperature on oxidation was studied to determine the existence of any structural differences appearing at different temperatures. The spectra are shown in Figure 11 for purified GR-S samples. These reactions were carried out in the absence of light at 55 and 100° C. Another sample was reacted at room temperature for a period of 5 months, during which no structural changes were observed. For the other two samples, the structural changes observed in the spectra appear

to be similar. There is, however, a considerable difference in the time required for about the same extent of oxidation. The similarity of the observed structural changes in these samples at different temperatures was one of the factors that led to the conclusion that in the initial stages of the oxidation reaction the rate of formation and decomposition of the hydroperoxides is about equal in this temperature range. This results in a net hydroperoxide concentration so low that it cannot be detected spectrally. Therefore, one cannot hope to detect, by means of the infrared spectrum, the formation of the hydroperoxides in the initiating oxidation reactions, which is postulated in current theories of autoxidation.

Along with the temperature studies, a series of experiments were conducted in which various antioxidants were introduced into the pure polymer. The antioxidants were the following: phenyl-2-naphthylamine, ditertiary butyl-*p*-

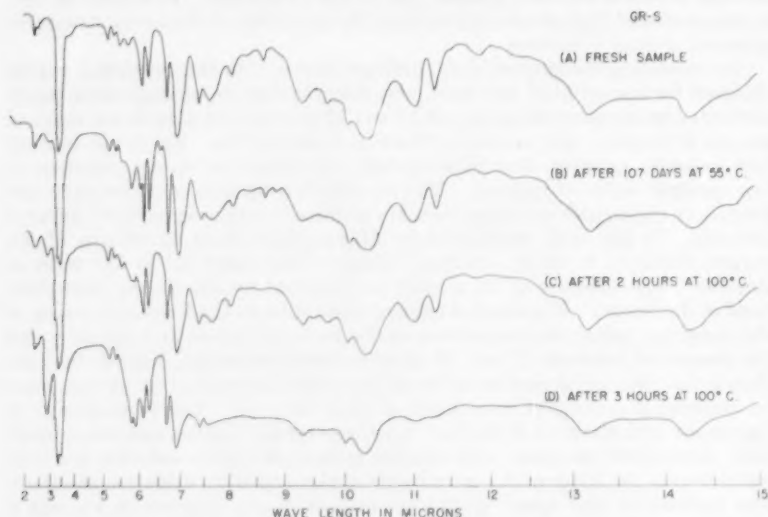


Fig. 11.—Spectral changes with oxidation at different temperatures.

cresol, diphenyl-*p*-phenylenediamine, hydroquinone benzyl ether, and tri-phenyl phosphite. The spectral results show that, in general, the structural changes produced by thermal oxidation are no different in the polymers containing antioxidant than in those without. There did seem to be a tendency for the carbonyl structures to appear before the hydroxyls, but whether or not this is significant has not yet been determined.

Since it is known that iron accelerates the oxidation reaction, the infrared spectra of pure polymers in which iron stearate had been introduced were examined. The concentrations used were 0.0003, 0.0017, and 0.01 per cent iron based on the polymer. The structural changes were followed in the absorption spectrum as the oxidation progressed in two series of samples, one of which contained no antioxidant and the other of which contained 1.25 per cent phenyl-2-naphthylamine. The reactions were carried out in the absence of light at 100° C.

In the polymer with no antioxidant, where observations could be obtained at the initial appearances of oxidation products in the spectrum, the hydroxyl and carbonyl structures arise simultaneously. The effect of the presence of iron in accelerating the oxidation reactions is illustrated in Figure 12. The extent of the oxidation with variation of iron content is shown for the same reaction time. The characteristic general absorption is clearly evident in the 10-micron region with new bands appearing at about 13.7 and 13.9 microns.

On the other hand, for the sample to which phenyl-2-naphthylamine has been added with the iron, the carbonyl structures appear for a considerable period of time before the hydroxyl structures as oxidation progresses. This is shown in Figure 13, where, at the end of 43 days' reaction time, the carbonyl

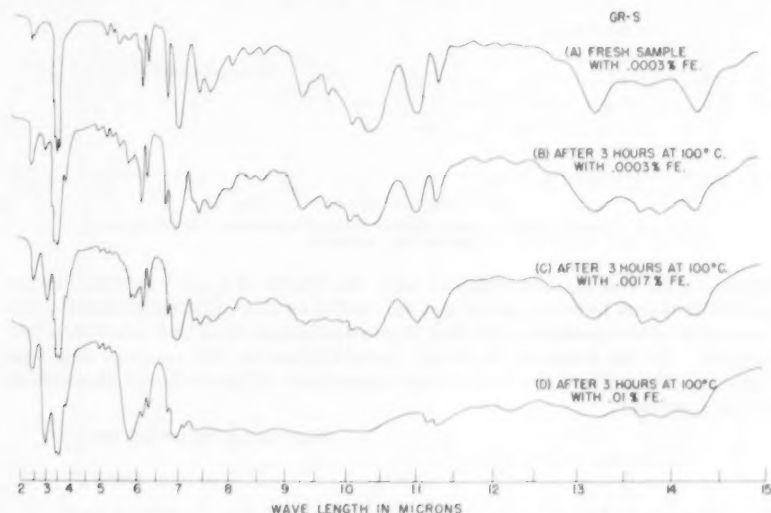


FIG. 12.—Spectral evidence of accelerating effects of iron on the oxidation of GR-S.

band at 5.8 microns has considerable intensity, with scarcely any evidence of hydroxyl absorption at 3 microns. At the end of 61 days' reaction, both structures show intense bands.

The progress of this reaction was followed more closely in the polymer sample containing 0.01 per cent iron with the antioxidant. These spectra are shown in Figure 14. The carbonyl band was first detected in the spectrum in a little less than 2 days' reaction time, as shown in Figure 14(B). The extent of oxidation after 12 and 20 days is shown in Figures 14(C) and 14(D). The hydroxyl structures did not become evident in the spectrum until the reaction had continued for 20 days, and even after this period the intensity of this band is relatively weak compared to that of the carbonyl. There seems to be little experimental doubt that the oxidation mechanisms involved in the iron containing polymers with this particular antioxidant are different than what has been observed in the others which have been similarly studied. The fact that the carbonyl and hydroxyl structures arise simultaneously in the same polymer sample in the absence of this antioxidant leads one to conclude that the antioxidant alters the oxidation mechanisms in the presence of iron. A possible ex-

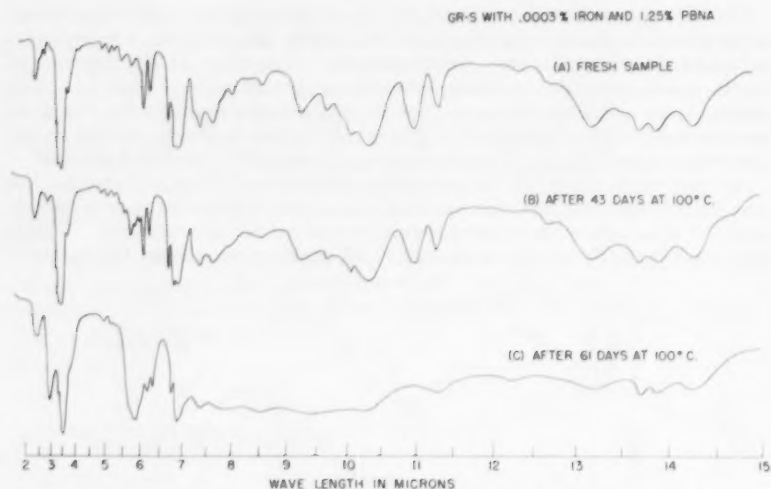


FIG. 13.—Spectral changes during oxidation of GR-S in presence of 0.0003 per cent iron and an antioxidant.

planation for this may be obtained from the results of Cook⁷, in which he reported that iron phthalocyanine not only acted as a catalyst for promoting the formation of the peroxides, but that it also accelerated their decomposition into ketones. In the presence of phenyl-2-naphthylamine, this reaction might be enhanced, thus giving rise to the initial appearance of the carbonyl absorptions in the spectrum.

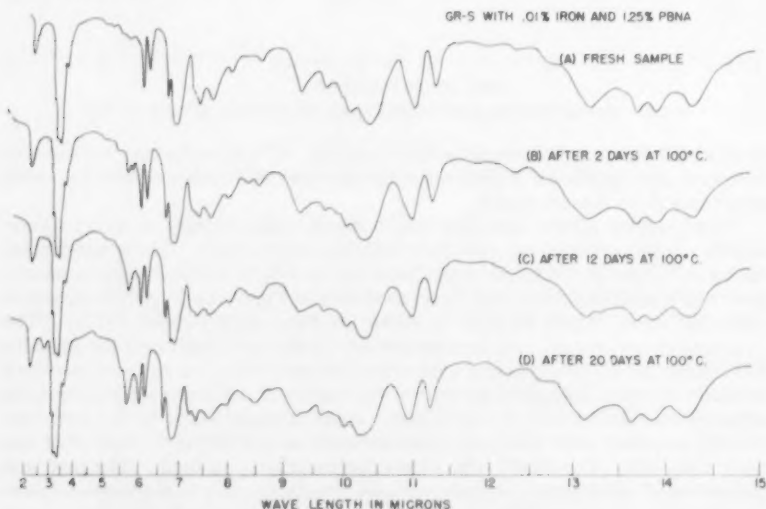


FIG. 14.—Spectral changes during oxidation of GR-S in presence of 0.01 per cent iron and an antioxidant.

EFFECTS OF ULTRAVIOLET RADIATION ON OXIDATION

The effect of ultraviolet light on initiating oxidation reactions in rubber has long been known. The absorption spectra were examined for structural changes in GR-S and polybutadiene at various stages of exposure to ultraviolet radiation. A Fadeometer was used as a source of such exposures.

Several butadiene polymers, containing no antioxidant, were examined for structural changes resulting from ultraviolet radiation. A typical spectroscopic result of such an examination is shown in Figure 15. In each case, the hydroxyl and carbonyl structures appear simultaneously after six to eight hours' exposure, become moderately intense after eleven to thirteen hours', and extremely intense after sixteen to twenty hours' exposure. The increased

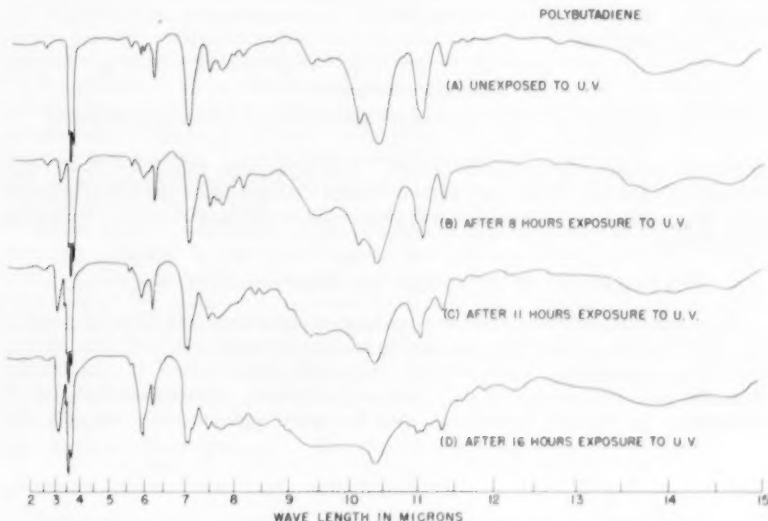


FIG. 15.—Effects of ultraviolet radiation on the infrared spectrum of polybutadiene.

absorption in the 10-micron region of the spectrum with increased oxidation is clearly shown in Figure 15.

The effects of ultraviolet radiation on GR-S polymers were investigated by introducing the same antioxidants that were used in the previous thermal oxidation studies. The spectra in Figure 16 illustrate the structural changes taking place under these conditions for one of these antioxidants. These spectra are also typical of other antioxidants. In all cases only a few hours' exposure was required to show structural changes, no changes being observed in the same polymer stored for 5 months in the absence of light at 55° C in an oxygen atmosphere. This is an indication that the antioxidants are not very effective in preventing oxygen attack on a polymer which is initiated by ultraviolet radiation. In the case of one antioxidant (phenyl-2-naphthylamine), the oxidation reaction was actually accelerated. This is shown in Figure 17, where the polymer sample containing the antioxidant required half the exposure time to bring out about the same extent of structural change in the spectrum

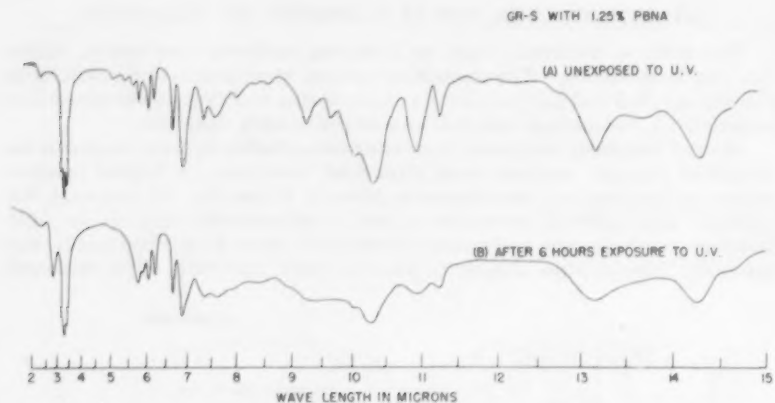


Fig. 16.—Effects of ultraviolet radiation on the infrared spectrum of GR-S with antioxidant.

as for the sample with no antioxidant. The consistent similarity in the absorption spectra of oxidized polymers indicates that oxidation reactions induced either thermally or by ultraviolet radiation result in similar structural changes in the polymer.

CORRELATION OF PHYSICAL PROPERTIES WITH SPECTRA

Some exploratory examinations have been made to correlate physical properties with oxygen absorption and the structural changes which appear in the absorption spectrum. Thus far the work has been limited to the tensile strength and elongation of unvulcanized, purified, antioxidant-free GR-S polymers. An Instron tester was used to make measurements on polymer

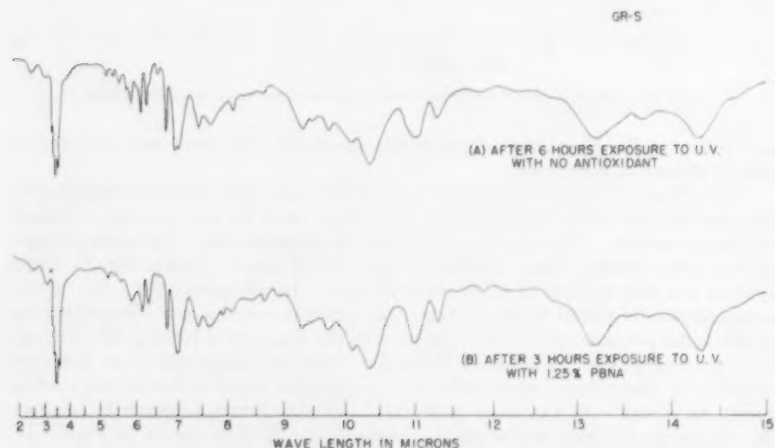


Fig. 17.—Spectra showing ineffectiveness of phenyl-2-naphthylamine in GR-S to prevent oxidation activated by ultraviolet radiation.

samples cut from the same thin films which were used for the spectral absorption examination.

Typical results of these measurements are given in Table I.

TABLE I
PURIFIED GR-S PHYSICAL PROPERTIES VS. OXYGEN ABSORPTION

Oxygen absorbed (%)	Tensile strength (lb./sq. in.)	Elongation (%)
0	15	1100-1600
2.4	15	1300
5	25	1500

It can be concluded from these results that no significant differences are indicated in these properties when up to 5 per cent oxygen has been absorbed by the polymer. No structural changes were observed in the absorption spectrum of the sample that absorbed 5 per cent oxygen.

In contrast to these results were those obtained with a film which had absorbed 2 per cent oxygen and was then exposed to ultraviolet light in a nitrogen atmosphere. The hydroxyl and carbonyl bands were very strong in the spectrum of this sample. The tensile strength increased from 25 lb. per sq. in. before exposure to ultraviolet light to 87 lb. per sq. in. while the elongation was reduced to only 10 per cent.

These experiments furnish a basis for believing that as long as the oxidation does not progress to the later steps of the reaction, which give rise to the hydroxyl and carbonyl groups, the physical properties are not much affected, even though the amount of combined oxygen is high. In consideration of the above data, it may be that effective protection of the physical properties against oxidation might be obtained equally well by inhibiting the reaction step which leads to hydroxyl and carbonyl compounds as by preventing the initial combination of oxygen. A study of vulcanized systems may be of interest in this connection. A few vulcanized samples have been examined, but no reliable data have yet been obtained. However, this is being pursued further.

CONCLUSIONS

It is a matter of considerable interest that polymers can combine with the large amounts of oxygen shown in these experiments, with so little evidence of this combination in the infrared spectrum. Either the oxygen must be distributed in a wide variety of types of compounds or it occurs in a type of linkage having low infrared absorption. In accordance with a previous discussion, it is reasonable to believe that a large proportion of these are ether linkages.

If, as has been postulated, the initial step in the autoxidation of hydrocarbons is the formation of hydroperoxides, it is not detected in the infrared spectrum. In order to conform to current theories on autoxidation, it must be assumed that the hydroperoxides formed in the initial oxidation reactions are decomposed at a rate about equal to their formation, so that their net concentration is always below the sensitivity of infrared observation. This does not appear to be an unreasonable assumption. Therefore, only the structures of the terminal products of the secondary reactions are believed to be observed in the infrared spectrum.

SYNOPSIS

Infrared absorption spectra were used to study the structural changes resulting from oxidation in a number of unvulcanized, purified polymers under a

variety of experimental conditions. The results showed that as oxidation progressed, the structural changes which were detected were qualitatively the same for all of the polymers under all these experimental conditions. Correlation of volumetric measurements with spectral data indicated that considerably more oxygen was absorbed by the polymer samples before structural changes could be detected than the minimum amount required for the initial detection of the hydroxyl and carbonyl structures. From the interpretation of information from the absorption spectrum, it is believed that the structural evidence is in substantial agreement with current theories on autoxidation. Although the initial hydroperoxide formation is not observed in the spectrum, it is probable that this reaction takes place with almost immediate decomposition, which results in a net hydroperoxide concentration so low as to make infrared methods insensitive for its detection. Correlation of physical properties with structural studies indicate that little change in these properties takes place until the hydroxyl and carbonyl structures become evident in the infrared spectrum.

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THE ROLE OF OXYGEN IN THE VULCANIZATION OF NATURAL RUBBER *

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A three-dimensional structure is formed during the vulcanization of rubber. The complex processes of formation, rupture, and regrouping of bonds during vulcanization lead finally to union of the long chain molecules into a compact network. The density of the network formed during vulcanization and the distribution and degree of sulfide formation by the bonds govern to a large degree the work-capacity of vulcanizates. Structure formation in vulcanizates is manifest by the change of their tensile strength, elasticity, swelling, and solubility.

During the vulcanization of natural rubber, an optimum is observed in the change of tensile strength and other technically important properties of the material. The decrease of tensile strength of vulcanizates by overvulcanization is usually ascribed to the oxidative destruction of the molecular chains of the rubber¹.

The strong influence which has been observed of oxygen on the tensile strength of natural rubber and its vulcanizates is the basic argument in favor of oxidative destruction. This influence, however, only appears when the rubber is in direct contact with oxygen or air. When, in the rubber industry, vulcanization is carried out in presses, the surface of the rubber mixture is isolated from atmospheric oxygen, and, consequently, destruction in this case can be caused only by the oxygen dissolved in the rubber mixture.

Can dissolved oxygen cause the destruction of rubber and thus influence notably the tensile strength of vulcanizates? In order to answer this question, we studied experimentally the direct oxidation of rubber in a press under the usual conditions of industrial vulcanization. The rate of oxidation of natural rubber was studied by its consumption of phenyl-2-naphthylamine². The rubber was purified by extraction with a methanol-acetone mixture in a current of purified nitrogen. Phenyl-2-naphthylamine (0.5 per cent) was added to the purified rubber.

The curves of consumption of phenyl-2-naphthylamine during heating at 143° C in a press in an atmosphere of oxygen are shown in Figure 1. Whereas the oxidation of rubber in oxygen is accompanied by intensive consumption of phenyl-2-naphthylamine, in a press no consumption of this inhibitor is observed. A small consumption of phenyl-2-naphthylamine is observed only in the molding operation, where the mold is in direct contact with atmospheric oxygen and is a barrier against the oxygen diffused in the rubber when in the press.

The study of the rate of oxidation by the rate of consumption of inhibitor still gives no idea of the change of properties of rubber during heating in a press. Furthermore, we can assume that stable rubber peroxides formed during plasticization, which have no influence on the rate of consumption of phenyl-2-

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naphthylamine, do, however, cause destruction of the rubber, by decomposing during further heating in the press.

The change of the structure of natural rubber during heating was studied by the change of viscosity of its solutions. Rubber at various stages of heating in a press was dissolved in benzene and brought to a concentration of 0.25 per cent. The viscosities of the solutions were then measured with an Ostwald viscometer (capillary diameter 0.3 mm.). The results are shown in Figure 2 (curves 1 and 2).

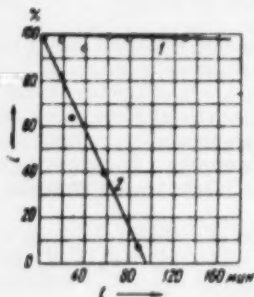


FIG. 1.—Consumption of phenyl-2-naphthylamine during heating of rubber hydrocarbon under various conditions at 143° C. 1. In a press. 2. In oxygen. ϵ is the concentration of phenyl-2-naphthylamine in rubber; t is the time of heating in minutes.

It should be noted that the change of viscosity of solutions of natural rubber is a very sensitive indication of its destruction. Nevertheless, we observed no fall of viscosity when rubber was heated for 180 minutes in a vulcanization press at 143° C.

Having observed no considerable oxidation of rubber, judged by the consumption of inhibitor or change in viscosity of the solutions, it then became necessary to activate the oxidation of the rubber by adding 0.5 per cent of

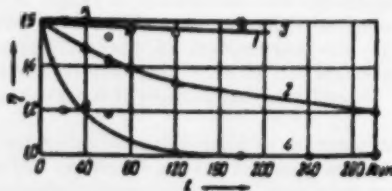


FIG. 2.—Change of relative viscosity of rubber solutions at various stages of heating at 143° C. 1 and 3. In a press. 2 and 4. In oxygen. 3 and 4. Oxygen activated by ferric naphthenate. η is the relative viscosity; t is the time of heating.

ferric naphthenate. This was added to plasticized rubber on a mill. The influence of this activated oxidation on the viscosity of rubber solutions is shown in Figures 2, 3, and 4.

In this case, too, there was no change of viscosity during the heating of rubber in a press. The activated process cannot develop because of the small concentration of oxygen in the rubber. When rubber is heated in oxygen, ferric naphthenate causes a tremendous change of viscosity of the rubber solutions.

Having shown that no perceptible oxidative destruction takes place in natural rubber during heating, it next had to be proved that such treatment has no influence on the mechanical properties of vulcanizates of natural rubber. For this purpose, plasticized natural rubber was heated in a press at 143° C for 20 minutes. This heated rubber was then vulcanized. The vulcanizate was composed of 100 parts by weight of natural rubber (smoked sheet); 3 parts of sulfur; 5 parts of zinc oxide; 0.5 part of stearic acid; and 0.7 part of mercapto-benzothiazole.

Data presented in Table 1 show that preliminary heating in a press has no noteworthy effect on the fundamental mechanical properties of vulcanized rubber. The slight difference in the values of the tensile strength and elongation of vulcanizates of untreated rubber and heated rubber lies within the limits of ordinary experimental error with a dynamometer and does not exceed 10 per cent.

TABLE 1
INFLUENCE OF PREVIOUS HEATING OF NATURAL RUBBER IN A PRESS ON
THE FUNDAMENTAL PHYSICAL-MECHANICAL PROPERTIES OF ITS
VULCANIZATES

Vulcanization (time in min.)	Tensile strength (kg. per sq. cm.)		Relative elongation (%)		Residual elongation (%)	
	not heated	after heating	not heated	after heating	not heated	after heating
10	197	227	790	790	6	5
20	225	192	802	785	8	8
30	211	216	762	808	8	9
40	218	200	804	795	9	8

The results shown above lead to the conclusion that oxidative destruction of rubber during vulcanization in a press is of no significance. Naturally the dissolved oxygen takes part in the oxidation of rubber. However, the process takes place at a continuously decreasing rate.

An approximate calculation, assuming that oxidation in this case follows a monomolecular law, since the concentration of double bonds of the rubber remains practically constant, shows that only one-twentieth as much oxygen is consumed in 1 hour of vulcanization as in the same period in air, while the number of points of destruction must decrease about ten times. Since the changes indicated are smaller than the limits of sensitivity of existing methods of analysis, they naturally cannot be detected.

It is known that antioxidants, e.g., secondary aromatic amines, have a considerable influence on the properties of vulcanized rubber. Evidently, in the light of the new data, this influence cannot be interpreted as an inhibiting action directed against the oxidative destruction of rubber.

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THE PROTECTION OF RUBBERS AGAINST OZONE CRACKING *

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INTRODUCTION

The cracking of stressed rubbers, which is clearly accelerated by traces of ozone in the air, is one of the most detrimental aspects of aging. Existing means of counteraction are still limited and of insufficient merit. The characteristic features of this cracking of rubber¹ are: (1) the necessity of a tension stress; (2) the presence in the rubber of particles capable of reacting with ozone, and (3) the surface nature of the process.

The fissuring of solid materials, e.g., metals², glass³, and plastic materials⁴, resulting from stresses (static fatigue) occurring along with certain deformations accompanied by tension, is well known. The fracturing is accelerated by repeated deformations and also by the influence of specific substances for each material under consideration⁵: humidity in the case of glass or brass; a solution of sodium chloride or alkali in the case of steel or aluminum; hydrofluoric acid in the case of nickel alloys⁶; an aqueous solution of saponin or a fat solution of oleic acid in the case of steel⁷, etc. The battle against the destruction of stressed materials in the presence of such specific factors not only aims to combat this phenomenon, which is dangerous in most cases, but also has practical applications; for example, in drilling (reducers, adsorption, hardness of the rock), mechanical treatment of metals⁸, polishing of glass and metals⁹, etc.

In the case of rubber, we have to deal both with the phenomenon of static¹⁰ or dynamic fatigue, i.e., cracking in the absence of ozone, and with the action of a specific substance which accelerates this cracking, namely, ozone. But whereas, in the case of solids which are subjected to stresses, fissuring and destruction are only relatively slightly accelerated by the action of specific substances, in the case of a normally vulcanized stretched rubber, the effect of ozone is to accelerate this fissuring appreciably. This is why, until now, the analogy between the mechanism of the fissuring of stressed solids and the cracking of rubber by ozone has not been studied.

This analogy is, nevertheless, verified by certain conformities in the two processes, such as the following:

1. When the temperature and stress are raised, the number of cracks definitely increases, while in each case their dimensions decrease.
2. A compression stress does not increase the ozone cracking either of rubber or of solids¹¹.
3. In each case, the elimination of a surface layer containing microcracks increases the resistance to fissuring¹².

* Translated from the *Revue Générale du Caoutchouc*, Vol. 31, No. 11, pages 898-900, November 1954, by D. M. Beach of the R. F. Goodrich Research Center. The paper in the *Revue Générale du Caoutchouc* is a French translation of the original paper in the *Doklady Akademii Nauk SSSR*, Vol. 93, No. 3, pages 483-486 (1953). This English version was generously contributed by the R. F. Goodrich Research Center, for which RUBBER CHEMISTRY AND TECHNOLOGY is very appreciative.

4. The quantitative equation for the time τ elapsed from the application of the stress σ to the point of rupture: $\log \tau = \alpha - \gamma \cdot \log \sigma$ (which is known for glass³ and plastic materials⁴, and whose theoretical basis has been given by Bartenev³), was also found valid by us in the case of the ozone cracking of pale crepe and cured Butyl rubber (Figure 1)¹².

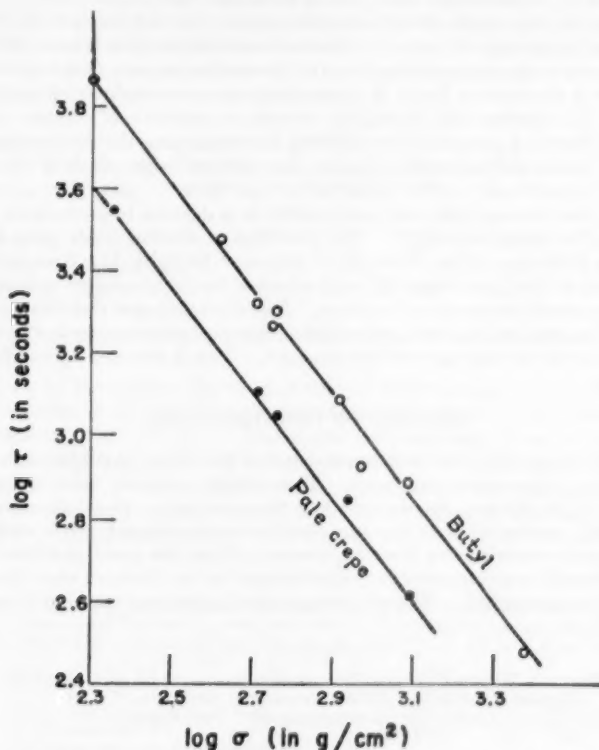


Fig. 1.—Time of cracking, as a function of the stress, of films of vulcanized pale crepe rubber and Butyl rubber. Ozone concentration 5×10^{-4} per cent for the pale crepe rubber and 10^{-2} per cent for the Butyl rubber.

Thus not only ozone, but also the stresses that are applied, play a prime role in the cracking of rubbers. The methods for protecting rubbers from ozone cracking may be arranged in the following groups:

1. The formation of a protective surface film: (a) by application of an ozone-resistant coating; (b) by introduction of substances which, by migrating to the surface of the rubber, form a continuous elastic layer; (c) by treatment of the surface of the rubber itself, so as to alter its chemical nature.
2. The lowering of the tension in the surface layer (or even in the interior) of the rubber.
3. The use of chemical protective agents, which completely neutralize the action of the ozone.

In current practice, Neoprene is used as an ozone-resistant coating, which has both advantages and disadvantages. Also waxy substances, when added to rubber, spread to the surface of the product and form a protective film¹⁴. This film protects rubbers to some extent during static deformation, but it does not generally protect them during dynamic deformation (unless this is accompanied by considerable heat, which melts the wax).

In view of the stress effects indicated above, we had recourse to two procedures for protecting rubbers: (1) diminution of the tension (source of cracks); (2) application of a compression stress to the surface layer. One way to reduce the stress in the surface layer, it seems, is to expose certain stretched rubbers to light. It is known that, during the process of oxidation of rubbers subjected to stress, there is a progressive weakening accompanying the diminution of this stress¹⁵. Under the influence of light, this process takes place in the surface layer, as is confirmed by the behavior of thin films¹⁶. Actually, exposure of stretched Neoprene rubbers to light results in a definite improvement of their resistance to ozone cracking¹⁷. We observed a similar effect with SKN-26 pure-gum rubbers. After three days' exposure to light, the time before the appearance of the cracks was 15 to 50 minutes for the stretched rubbers¹⁸, and 50 minutes for the unstretched rubbers. The diminution of the tension stresses may also be obtained by the application of compression stresses in the opposite direction in the surface layer of the product. This is effected by the following technique.

METHOD OF CONSTRUCTION

Samples were prepared which consisted of flat slabs of rubber adhered together as a three-layer sandwich. The middle slabs, 1 mm. thick, were stretched 0, 10, 30 and 50 per cent and fixed as such. On both sides of the middle slab, similar slabs of the same rubber were adhered, 1.05, or 0.3 mm. thick. After removing the three-layer sample from the press, the two surfaces were subjected to a compression proportionate to the distance that the middle slab had been stretched. The unstressed middle slab was taken as a standard.

TABLE I
TIME IN MINUTES WHICH ELAPSED BEFORE THE APPEARANCE OF CRACKS ON THREE-LAYER SAMPLES OF SKB (THICKNESS OF SLABS, 0.5 MM.; OZONE CONCENTRATION, 10^{-2} PER CENT)

Nature of deformation	Percentage stretch of middle slab			
	0	10	30	50
Static (15 per cent)	25	25	105	180
Dynamic	50	65	80	100

The samples were then exposed to the action of ozone, with 25 per cent static stretch, or with dynamic deformation (at 78 deformations per minute and 25 per cent stretch). The results of the experiments with SKB-rubber are given in Table I.

Table I shows that the application, before stretching the sample, of a compressive force to the surface layer increases considerably the resistance of the rubber to ozone cracking. This effect lasts for 30-40 days after preparation of the samples. Similar results were obtained with three-layer samples, whose outside slabs were 0.3 mm. thick, and also with three-layer samples of SKS-30 rubber and Neoprene.

Cylindrical samples of SKS-30 rubber¹ (diameter 40 mm., thickness of wall 1.4 mm.) and SKB rubber² (diameter 46 mm., thickness of wall 2.8 mm.) were vulcanized and then cut along the axis and joined together by the inner surface. The result was a flat slab composed of two bands, both of which were compressed 3-4 per cent for the SKS-30, and 5-6 per cent for the SKB. Tests of these samples showed considerable improvement in their resistance to ozone cracking. Table II gives the result of the experiments with two-layer samples of rubber, for SKS-30 and SKB, which were bent into tubes of 3 cm. diameter for the SKS-30 and 4 cm. diameter for the SKB. The tests were made ten to fifteen days after the preparation of the samples.

TABLE II
TIME ELAPSED (IN MINUTES) TO THE POINT OF CRACKING
OF THE TWO-LAYER SAMPLE

Experimental conditions	Samples*					
	3N	3P	3V	1N	1P	1V
Ozone 5×10^{-4} per cent + light	—	—	—	32	—	200
Ozone 10×10^{-4} per cent	11	22	132	40	—	70
Ozone 3.7×10^{-3} per cent	—	—	—	10	20	85

* The letter V denotes samples joined by the inner surface; N, by the outer surface; P, two-layer samples from a flat slab.

Swelling of the surface layer of rubber in high boiling liquids (castor oil, triethanolamine, etc.) results in a definite improvement in its resistance to ozone cracking during dynamic and static deformations, provided that compression has been applied to this layer (Table III). Nevertheless, this effect is temporary and it disappears one or two days after the dilation because of the loss of compression caused by the diffusion of the liquid, which migrates from the surface layer to the interior of the sample.

TABLE III
EFFECT OF TREATMENT WITH SWELLING AGENTS AT THE BOILING POINT ON THE ELAPSED
TIME (IN MINUTES) BEFORE OZONE CRACKING OF RUBBERS SUBJECTED TO DYNAMIC
DEFORMATIONS. OZONE CONCENTRATION, 6×10^{-4} TO 3×10^{-3} PER CENT.

Swelling agent	SKB standard type	SKB 109 parts of carbon black per 100 parts of latex	SKS-30 standard type
No treatment	12	4	14
Triethanolamine	25	40	—
Castor Oil	—	100	145
DCA	>320	>300	>200

It is possible to prolong the compression stresses produced in the swelling treatment by changing the nature of the surface layer. For example, treatment of 75 per cent SKB rubbers with sulfuric acid and their subsequent dilation in triethanolamine assures protection for several months of dynamic deformations (Table IV).

From an analogy between the process of fissuring of solids and that of cracking of rubber by ozone, it might be supposed that the application of compressive forces would be equally applicable to the protection of solids. Actually, methods have been described in the technical literature for increasing the resistance of metals to fissuring by surface rolling and shot-blasting¹¹, and of glass by tempering¹².

TABLE IV
EFFECT OF DIFFERENT TREATMENTS OF RUBBERS ON THEIR
RESISTANCE TO OZONE CRACKING

Rubber from latex	Conditions of treatment	Time elapsed before cracking (minutes)	
		Light, ozone, static deformation	Ozone, dynamic deformation
SKB	Without treatment	10	10
	H ₂ SO ₄	30	10
	Triethanolamine	16	20
	H ₂ SO ₄ , triethanolamine	600	380
SKS-30	Without treatment		10
	H ₂ SO ₄		17
	H ₂ SO ₄ , triethanolamine		330
	H ₂ SO ₄ , castor oil		120

The possibility of applying such methods to rubbers to protect them against cracking, in the same way as to solid materials, confirms once more the similarity of the fissuring processes in the two cases.

SUMMARY

The paper describes a study of the aging of natural rubber and synthetic rubbers by the action of ozone. Ozone promotes the development of cracks under tension. The cracking does not occur under compressive stress, a fact which suggests a means of protection, namely, precompression. Another suggestion is the formation of a resistant surface layer that is insensitive to the action of ozone, such as Neoprene. Experiments based on these recommendations are described. A practical method of obtaining precompression is to distend the surface of the rubber with suitable swelling agents, such as triethanolamine. The effect is analogous to the shot-blasting treatment used for prestressing metals to protect them from fatigue cracking.

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- ¹⁸ PRK-7 lamp, with light filter placed about 4 cm. from the center of the lamp; temperature about 30° C. The test of resistance to ozone cracking was done with samples stretched 30 per cent by static stresses, and with a concentration of ozone of 8×10^{-4} per cent.
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JOINT INFLUENCE OF FREE AND COMBINED SULFUR AND OF *N*-PHENYL-2-NAPHTHYLAMINE ON THE OXIDATION OF VULCANIZED RUBBER *

A. S. KUZMINSKIĬ AND S. I. BASS

The fundamental theories of oxidation of rubbers have been developed in recent years, and many of our own studies have been devoted to the mechanism of this process¹. The laws observed in the oxidation of rubbers cannot be applied directly to mixtures which contain various ingredients besides rubber.

It has been established² that nearly all the ingredients in rubber influence the oxidation of the rubber itself, by reacting with the active centers of the rubber and, by taking part in the inhibition and chain transfer. It has also been established that the effects of the ingredients is not additive; they influence each other, and take part in the development of the oxidation process of the rubber component in the mixture.

In the present work, one of the most difficult problems of rubber oxidation is considered, i.e., the role of free and combined sulfur in the oxidation of vulcanized rubber.

This study is one stage in our investigations of the oxidation of rubber, and does not pretend to treat the problem exhaustively or from all aspects.

There are very few data in the scientific literature on the problem of the influence of free and combined sulfur on the oxidation of vulcanized rubber, and such data as are available are often contradictory.

As for free sulfur, a number of investigators agree that it is an inhibitor at low temperatures and a chain transfer agent at high temperatures³.

The role of combined sulfur in oxidation processes has not yet been explained. Boggs and Blake⁴ and Kohman⁵ regard sulfur as a cause of more rapid aging, while Shelton and Winn⁶ adhere to the opposite view. We have previously shown that combined sulfur in concentrations up to 0.5 per cent has no influence on the rate of oxidation of vulcanized rubber. The joint influence of Neozone and free sulfur on oxidation was explained with respect to rubber in one of our studies², where a number of specific properties in the behavior of sulfur and *N*-phenyl-2-naphthylamine were discussed for a rubber-sulfur-*N*-phenyl-2-naphthylamine-oxygen system. There are no data of the influence on oxidation of combined sulfur in the presence of *N*-phenyl-2-naphthylamine.

The purpose of this study is an explanation of the influence of free and combined sulfur, as well as their combination with *N*-phenyl-2-naphthylamine, on the oxidation of vulcanized rubber.

EXPERIMENTAL PART

Vulcanizates of commercial sodium-butadiene-rubber containing no *N*-phenyl-2-naphthylamine, obtained by liquid-phase polymerization, and having a Karrer plasticity of 0.51, were used in these experiments.

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Zhurnal Prikladnoi Khimii*, Vol. 27, No. 2, pages 189-197 (1954).

The following simple recipe was used (in parts by weight): rubber 100, sulfur 3, *N*-phenyl-2-naphthylamine 1. The mixtures were vulcanized in an electric press at 180° C.

The vulcanization times were 10 and 15 minutes, corresponding to a free sulfur content approximately 0.15 and 0.015 per cent for a constant total percentage of sulfur. The thickness of the films was 0.2 mm.

The rate of consumption of *N*-phenyl-2-naphthylamine and sulfur, and the rate of absorption of oxygen were studied. In order to determine the structural changes which take place in vulcanizates during oxidation, the equilibrium high-elastic modulus was determined; this is in the 3/2 degree directly proportional to the density of the spatial network of the vulcanizate. The apparatus and method were described in several of our previous works⁷. It should be

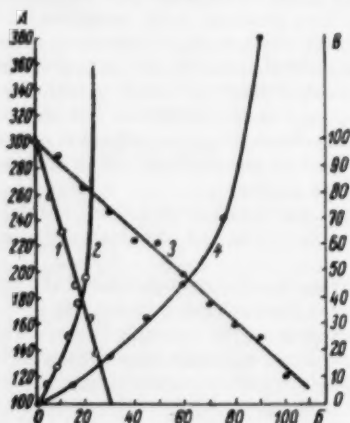


Fig. 1.—Kinetics of consumption of sulfur and change of equilibrium modulus during oxidation. Left-hand ordinate.— E_{00}^3 value of the equilibrium modulus (in per cent of original). Abscissa. Time (in hours).

Right-hand ordinate.—Concentration of free sulfur (per cent of original).

Curve 1.—Consumption of sulfur at 100° C (original concentration of free sulfur 0.16 per cent). Curve 2.—Change of modulus at 100° C. Curve 3.—Consumption of sulfur at 80° C (original concentration of free sulfur 0.14 per cent). Curve 4.—Change of modulus at 80° C.

mentioned that the concentration of free sulfur was determined by the method of Bolotnikov and Gurova⁸, and the equilibrium modulus, at a constant deforming force.

The results of the experiments proved satisfactorily reproducible.

The discrepancy between parallel experiments on oxygen absorption was 5 per cent, for a consumption of *N*-phenyl-2-naphthylamine of 6 per cent, for a sulfur consumption of about 20 per cent, and for a change of equilibrium modulus of 8–10 per cent.

Influence of free and combined sulfur on the oxidation of vulcanizates.—The curves of the change of the equilibrium modulus and the kinetics of consumption of free sulfur during oxidation at 80° and 100° C are shown in Figure 1.

It is seen from these data that free sulfur is consumed linearly throughout the oxidation process. The values of the equilibrium modulus change uniformly at first, and then a sharp rise is observed, due to the development of autocatalytic oxidation. The bend in the curve of change of equilibrium modu-

lus is evidently caused by the sharply increased rate of oxidation. About 30 per cent of the free sulfur remains in the system at this moment.

The fact that the rate of consumption of sulfur does not change even after the beginning of autocatalysis, when the concentration of active oxygen centers increases many times over, proves that the sulfur reacts only with a certain part of the active centers (probably the initial ones).

The influence of various concentrations of free sulfur on the kinetics of change of the equilibrium modulus during oxidation at 100° C is shown in Figure 2. The higher is the concentration of free sulfur, the later is the deflection of the curve, but the denser is the spatial structure.

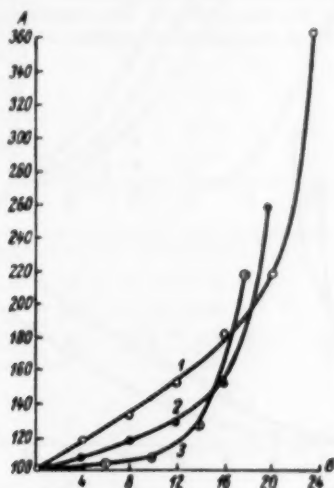


Fig. 2.—Influence of free sulfur on the kinetics of change of equilibrium modulus at 100° C.
Ordinate.— $E_{\infty}^{1/2}$ value of equilibrium modulus (per cent of original).
Abcissa.—Time (in hours).
Sulfur vulcanizates containing free sulfur.

Curve 1.—0.16 per cent
Curve 2.—0.024 per cent
Curve 3.—No free sulfur

Data for a vulcanizate from which the free sulfur had been eliminated by prolonged extraction (65 hours) with acetone are shown for comparison. The corresponding curve has a much greater slope, and the deflection appears earlier than when free sulfur is present. For a system containing 0.16 per cent of free sulfur, the increase of the equilibrium modulus was 236 per cent at the deflection on the $E_{\infty}^{1/2}$ -time curve, and the deflection appeared 20 hours after the beginning of oxidation. For a vulcanizate containing 0.024 per cent of free sulfur, the increase is 150 per cent at the moment of deflection, and the deflection appears 16 hours after the beginning of oxidation; for a vulcanizate without free sulfur, the increase is 125 per cent, and the deflection appears 12 hours later. Thus the greater is the content of free sulfur, the denser is the structure formation which it causes.

An analogous picture was observed at 120°, 130°, and 150° C. The influ-

ence of the original concentration of free sulfur on the kinetics of absorption of oxygen at 120° C is shown in Figure 3.

It is seen from the data presented that the higher is the concentration of free sulfur in the original specimen, the longer is the induction period and the steeper is the slope of the kinetic curve of oxygen absorption. The change of equilibrium modulus during oxidation is shown in the same figure. The beginning of appreciable oxygen absorption corresponds to the moment of deflection of the curve of change of equilibrium modulus. This was observed at all the temperatures studied.

In order to explain the influence of combined sulfur alone on oxidation, a heat vulcanizate was prepared with a network density equal to that of a sulfur vulcanizate containing no free sulfur. The expression "heat vulcanizate" refers to the products of heat conversion of rubber without vulcanizing agents.

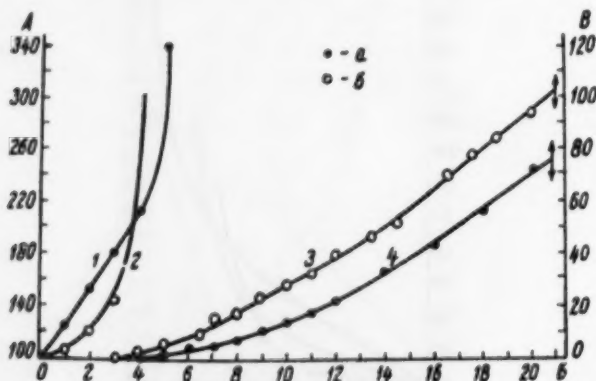


Fig. 3.—Influence of free sulfur on the kinetics of absorption of oxygen and change of equilibrium modulus at 120° C.

Left-hand ordinate.— E_{∞} value of equilibrium modulus (per cent of original). Abscissa.—Time (in hours). Right-hand ordinate.—Quantity of oxygen absorbed (millimol./mol.). Curves 1 and 2.—Change of modulus. Curves 3 and 4.—Absorption of oxygen.

Original concentration of free sulfur: a.—0.14 per cent. b.—0.013 per cent.

Sulfur vulcanizates are products obtained from the action of heat on rubber with sulfur present as a vulcanizing agent.

The corresponding data for the kinetics of oxygen absorption at 130° C are presented in Figure 4.

Combined sulfur changes radically the oxidation picture. Although the initial rate of oxidation of a heat-vulcanizate differs little from that of raw rubber, in sulfur vulcanizates containing approximately 3 per cent combined sulfur (no free sulfur), it is 15–20 times less.

Free sulfur without combined sulfur added to a heat vulcanizate during swelling in a benzene solution of sulfur in the same concentration, i.e., three per cent, gives a much greater effect for a heat vulcanizate, and it causes the appearance of an induction period of 14 hours.

Joint influence of sulfur (free and combined) and N-phenyl-2-naphthylamine on the oxidation of vulcanizates.—The joint action of free sulfur and N-phenyl-2-naphthylamine on the oxidation of rubber is not additive, and it depends on the

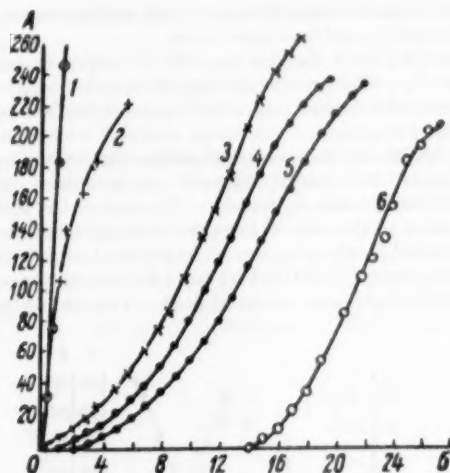


FIG. 4.—Influence of free and combined sulfur on the kinetics of oxidation at 130° C.
 Ordinate.—Quantity of oxygen absorbed (millimol./mol.).
 Abscissa.—Time (in hours).

Vulcanizates 2, 3, 4, 5, and 6 had $E_m = 12$ kg. per sq. cm.).

Curve 1.—Pure rubber. Curve 2.—Heat vulcanizate.
 Curve 3.—Sulfur vulcanizate without free sulfur.
 Curve 4.—Sulfur vulcanizate with 0.016 per cent free sulfur.
 Curve 5.—Sulfur vulcanizate with 0.128 per cent free sulfur.
 Curve 6.—Heat vulcanizate with 3 per cent free sulfur.

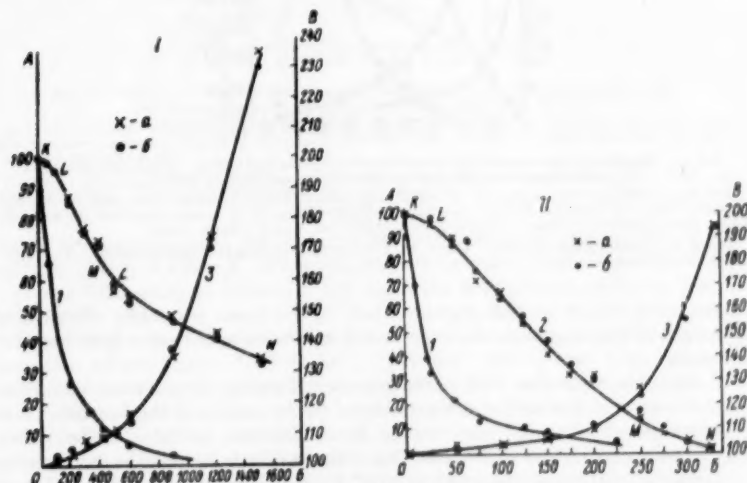


FIG. 5.—Kinetics of consumption of phenyl-2-naphthylamine and change of equilibrium modulus during oxidation at 80° C (I) and at 100° C (II).

Left-hand ordinate.—Concentration of phenyl-2-naphthylamine and sulfur (in per cent of original values).
 Abscissa.—Time (in hours).

Right-hand ordinate.—Value of equilibrium modulus $E_m^{1/3}$ (per cent of original value).
 Concentration of free sulfur (%). I. a.—0.017, b.—0.131; II. a.—0.02, b.—0.16.

temperature and relative concentration of both antioxidants². These rules are only partly applicable to sulfur vulcanizates.

As is seen from Figure 5 (Section I), at 80° C sulfur is consumed intensively in the first hours of oxidation, whereas hardly any *N*-phenyl-2-naphthylamine is consumed during this period (segment K-L). After 200 hours of oxidation, the rate of sulfur consumption decreases sharply, while that of *N*-phenyl-2-naphthylamine begins to increase noticeably (linear segment L-M on the curve). When these two initial segments are extended, the values of the equilibrium modulus increase uniformly. The end of the linear segment L-M is due to an increase of the rate of increase of the equilibrium modulus. This deflection is observed in the presence of 50 per cent of free *N*-phenyl-2-naphthylamine in the system. The third segment M-N on the curve of consumption of *N*-phenyl-2-naphthylamine is curvilinear. The amine concentration de-

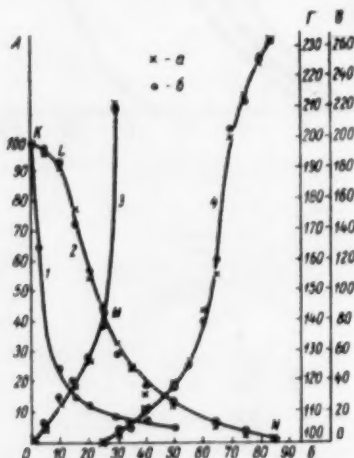


Fig. 6.—Kinetics of consumption of phenyl-2-naphthylamine and sulfur. Absorption of oxygen and change of equilibrium modulus during oxidation at 120° C.

Left-hand ordinate.—Concentration of sulfur and phenyl-2-naphthylamine (per cent of original). Abscissa.—Time (in hours). Extreme right-hand ordinate.—Quantity of oxygen absorbed (in millimol./mol.). Inner right-hand ordinate.—Equilibrium modulus (per cent of original value).

Curve 1.—Consumption of sulfur. Curve 2.—Consumption of phenyl-2-naphthylamine. Curve 3.—Change of equilibrium modulus. Curve 4.—Free sulfur content (%). a.—0.014, b.—0.123.

creases much slower on this segment than on the linear segment. Because of the length of this segment, the experiment was interrupted after 1500 hours of oxidation.

It should be remarked that, in the presence of amine, the influence of various concentrations of free sulfur is not reflected in the course of the kinetic curves of consumption of amine and change of equilibrium modulus. The points corresponding to various concentrations of free sulfur fall along the same curve.

A similar picture is observed at 100° C. The deflection of the curve of change of equilibrium modulus here, too, corresponds to the passage from a linear segment to a curvilinear one on the curve showing the *N*-phenyl-2-naphthylamine consumption.

The kinetics of consumption of *N*-phenyl-2-naphthylamine and sulfur, and

the kinetics of oxygen absorption and change of equilibrium modulus at 120° C, are shown in Figure 6.

A sharp deflection of the curve of change of equilibrium modulus and passage from the linear to the curvilinear segment of the curve of consumption of *N*-phenyl-2-naphthylamine correspond to the time of initiation of oxygen absorption.

Thus, there is a complete correspondence between the change of equilibrium modulus, consumption of *N*-phenyl-2-naphthylamine, and oxygen absorption. At both 80° and 100° C autocatalytic oxidation develops in the presence of about 40 per cent of free *N*-phenyl-2-naphthylamine in the system. The laws of behavior of *N*-phenyl-2-naphthylamine and sulfur are the same at 80–100° C. At 130° C, a similar picture is observed (Figure 7). The concentration of free sulfur has no influence on the course of the kinetic curves. The kinetic curves of consumption of amine, change of equilibrium modulus, and absorption of

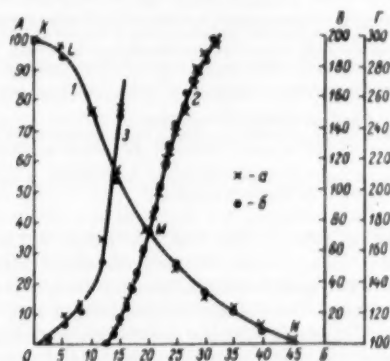


FIG. 7.—Kinetics of consumption of phenyl-2-naphthylamine. Absorption of oxygen and change of equilibrium modulus during oxidation at 130° C.

Left-hand ordinate.—Concentration of amine (per cent of original value). Abcissa.—Time (in hours). Inner right-hand ordinate.—Quantity of oxygen absorbed (millimol./mol.). Outer right-hand ordinate.—Equilibrium modulus $E_{w^{1/2}}$.

Curve 1.—Consumption of phenyl-2-naphthylamine. Curve 2.—Absorption of oxygen. Curve 3.—Change of modulus. Free sulfur content (%): a—0.011, b—0.155.

oxygen are superimposed for vulcanizates with different original free sulfur contents.

It was interesting to determine the influence of combined sulfur on the behavior of the amine.

Figure 8 shows curves of consumption of *N*-phenyl-2-naphthylamine and absorption of oxygen at 130° C for: (1) a heat vulcanizate with the same equilibrium modulus as the sulfur vulcanizate; (2) a sulfur vulcanizate, and (3) a sulfur vulcanizate from which the free sulfur has been eliminated.

As is seen from the data presented, in the heat vulcanizate, *N*-phenyl-2-naphthylamine is consumed linearly, and autocatalytic oxidation develops after all the free amine is exhausted. In the sulfur vulcanizate containing no free sulfur, the amine is also consumed linearly, but at twice the rate as in the heat vulcanizate. In this case, too, autocatalytic oxidation develops after all the *N*-phenyl-2-naphthylamine is exhausted, while, in the presence of the slightest amount of free sulfur (0.011 per cent), autocatalysis develops in the

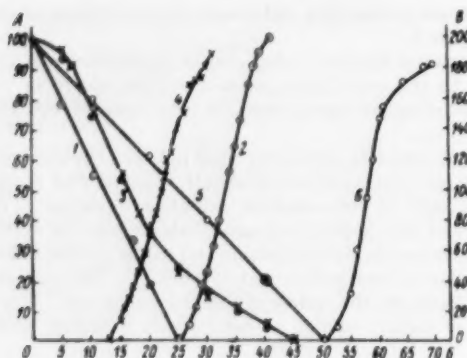


Fig. 8.—Influence of free and combined sulfur on the kinetics of consumption of phenyl-2-naphthylamine and absorption of oxygen at 130° C.

Left-hand ordinate.—Concentration of phenyl-2-naphthylamine (per cent of original). Abscissa.—Time (in hours). Right-hand ordinate.—Quantity of oxygen absorbed (millimol./mol.)

Curve 1.—Consumption of phenyl-2-naphthylamine by sulfur vulcanizate with $E_{\text{free}} = 12$ kg. per sq. cm. and without free sulfur.

Curve 2.—Absorption of oxygen of the same vulcanizate.

Curve 3.—Consumption of phenyl-2-naphthylamine for sulfur vulcanizate $E_{\text{free}} = 12$ kg. per sq. cm. and free sulfur content: (crosses) 0.155% and (circles) 0.011%. Curve 4.—Absorption for the same vulcanizate.

Curve 5.—Consumption for heat vulcanizate with $E_{\text{free}} = 12$ kg. per sq. cm.

Curve 6.—Absorption of oxygen for the same vulcanizate.

presence of about 40 per cent of the original amine concentration. Furthermore, in the presence of free sulfur, the rate of consumption of amine on the linear segment is greater than in the heat vulcanizate, and is almost equal to the rate of consumption in a sulfur vulcanizate containing no free sulfur.

Thus, combined sulfur accelerates the consumption of *N*-phenyl-2-naphthylamine, and free sulfur is responsible for the presence of two curvilinear segments of the consumption curve.

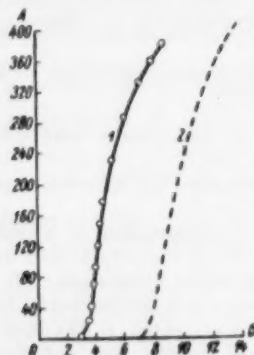


Fig. 9.—Kinetics of oxidation of rubber, prepared with phenyl-2-naphthylamine at 130° C amine concentration 0.275 per cent.

Ordinate.—Quantity of oxygen absorbed (millimol./mol.). Abscissa.—Time (in hours).

Curve 1.—Oxygen absorption by rubber prepared with phenyl-2-naphthylamine, extracted from oxidized sheets.

Curve 2.—Oxygen absorption by rubber prepared with pure phenyl-2-naphthylamine in the same concentration.

Since, in the presence of free sulfur, autocatalytic oxidation develops if there is a relatively high proportion of *N*-phenyl-2-naphthylamine in the system, it would be natural to assume that the amine remaining in the system at this moment loses most of its inhibiting power.

In order to verify this assumption, the oxidation of rubber containing *N*-phenyl-2-naphthylamine which remained in a vulcanizate at the beginning of autocatalytic oxidation was studied experimentally. The corresponding curve is shown in Figure 9. For purposes of comparison, the broken curve of absorption of oxygen by rubber containing pure *N*-phenyl-2-naphthylamine in the same concentration is also shown.

It is seen from these data that the amine which remains at the beginning of autocatalysis has about half the inhibiting power of the pure amine.

INTERPRETATION OF THE RESULTS

The results described in the experimental part show that both free and combined sulfur retard oxidation processes in rubber, in the absence of *N*-phenyl-2-naphthylamine. The inhibiting action of free sulfur on the oxidation of vulcanizates shows several peculiarities. Free sulfur is a weak inhibitor. Joining in the oxidation process, it causes intensive additional structure formation beyond that caused by oxygen. The higher is the initial concentration of free sulfur, the longer is the induction period, but the more does the density of the spatial network increase during oxidation.

It should be added that there is a complete correspondence between the change of equilibrium modulus and the beginning of autocatalytic oxidation; the deflection of the curve of the change of equilibrium modulus corresponds to the beginning of apparent absorption of oxygen.

Combined sulfur also has an essential influence on the development of oxidation processes. It was shown in the experimental part that the rate of oxidation of a sulfur vulcanizate containing no free sulfur at 130° C is 15–20 times less than the rate of oxidation of a heat vulcanizate with the same initial density of network.

It would seem that the inhibiting action of combined sulfur in the particular vulcanizates studied can be explained as follows. It is known that polysulfide sulfur is the principal product formed during vulcanization without accelerators and with sulfur as the vulcanizing agent. This form of sulfur is bound much more weakly than is monosulfide sulfur in the vulcanized structure. During oxidation, a part of the polysulfide bonds is decomposed, with liberation of active sulfur. The latter (probably in the form of sulfur-bearing radicals) can react with the hydrocarbon radicals, double bonds, or oxygen. In the latter case, the oxidizing chains are much shorter than in the absence of sulfur. This is one cause of the decrease of the rate of oxidation in the case of the sulfur network in comparison with the hydrocarbon network. Thus, the action of bound polysulfide sulfur is similar to that of free sulfur.

The great effectiveness of free sulfur (the long induction period at 130° C) in a concentration equal to that of combined sulfur is caused on the one hand by the low mobility of the decomposition products of polysulfide sulfur in comparison with free sulfur. On the other hand, the concentration factor plays an important part. In fact, in this case, the concentration of polysulfide sulfur is less than the total concentration of combined sulfur and, besides, it is evidently not all destroyed during oxidation. Thus the effective concentration of combined sulfur is much less than the measured difference between the total concentration of sulfur and the concentration of free sulfur.

It follows from the data obtained for the whole temperature range that, in rubber too, the free sulfur replaces the *N*-phenyl-2-naphthylamine, preventing its consumption in the early stages of oxidation. This is evidently due to the greater activity of sulfur compared to the amine with respect to the radicals formed as a result of oxidation. The new sulfur-bearing radicals are not sufficiently active to break off a hydrogen atom from the *N*-phenyl-2-naphthylamine molecule, but are able to carry the chain initiated by the oxygen.

It should be remembered that the rate of consumption of sulfur in the presence of *N*-phenyl-2-naphthylamine is less than in its absence. Since *N*-phenyl-2-naphthylamine is consumed in the first hours of oxidation, although slowly, and reacts with a part of the radicals formed as a result of oxidation, the fraction of these radicals combining with the sulfur will decrease, causing a decrease of the rate of consumption of the sulfur. At all the temperatures studied, there is also a correspondence between the change of the equilibrium modulus and the course of the oxidation processes in the vulcanizate. This shows that the kinetics of change of the equilibrium modulus during oxidation reflects accurately the accompanying physical-chemical changes in vulcanizates.

As has already been demonstrated, at all the temperatures studied, various concentrations of sulfur in the presence of *N*-phenyl-2-naphthylamine have no effect on the course of the kinetic curves of consumption of *N*-phenyl-2-naphthylamine, absorption of oxygen, and change of equilibrium modulus. It is evident that slight amounts of free sulfur are sufficient to cause the phenomena described. This can also be a result of the specific influence of combined sulfur (which is much greater in these cases than that of free sulfur) on oxidation in the presence of *N*-phenyl-2-naphthylamine. In view of this, differences in the concentration of free sulfur are not reflected in the development of the oxidation processes.

Combined sulfur, which represents the sulfur network, accelerates the consumption of *N*-phenyl-2-naphthylamine in comparison with a heat vulcanizate. This is evidently dependent on the fact that the products of the decomposition of polysulfide sulfur (as contrasted with free sulfur) are active enough to react with *N*-phenyl-2-naphthylamine. Indirect proof of this theory is the following. As was shown above, combined sulfur in the absence of *N*-phenyl-2-naphthylamine retards greatly the absorption of oxygen. In this case it acts like free sulfur, that is, it inhibits oxidation (see Figure 4).

In the presence of *N*-phenyl-2-naphthylamine, the products of the decomposition of polysulfide sulfur react with the latter and no longer have any inhibiting effect on oxidation. In fact, the slope of the curve of oxygen absorption for a sulfur vulcanizate containing *N*-phenyl-2-naphthylamine, but containing no free sulfur, does not differ from the slope of the corresponding curve for a heat vulcanizate containing the same proportion of *N*-phenyl-2-naphthylamine (see Figure 8).

For rubber containing free sulfur², the rate of consumption of *N*-phenyl-2-naphthylamine in the linear segment (when almost all the free sulfur is already bound by the oxygen) is less than the rate of consumption of *N*-phenyl-2-naphthylamine in the absence of free sulfur. In sulfur vulcanizates, this rate is much higher than in a heat vulcanizate of the same density of network.

Thus sulfur bound by oxygen retards the consumption of *N*-phenyl-2-naphthylamine, while sulfur combined during vulcanization sharply accelerates the consumption of *N*-phenyl-2-naphthylamine, and leads to a shortening of the induction period. These facts indicate that the influence of combined sulfur on oxidation depends on its structure.

CONCLUSIONS

1. A study of the influence of free and combined sulfur on the development of oxidation processes in vulcanizates in the temperature range of 80–130° C showed a complete correspondence between the structural changes and chemical processes during the oxidation of vulcanizates.

2. Free sulfur in vulcanizates is not only a weak inhibitor but a detrimental one, since, in addition to a slight lengthening of the induction period, it causes dense structure formation. Combined, i.e., polysulfide, sulfur in the absence of *N*-phenyl-2-naphthylamine has an inhibiting effect on oxidation.

3. Free sulfur inhibits the protective action of *N*-phenyl-2-naphthylamine and, consequently, has a harmful effect on oxidation at high temperatures. Combined sulfur is also harmful at high temperatures, since it causes unproductive consumption of amine, and thereby greatly shortens the induction period in comparison with that of a heat vulcanizate.

4. In the presence of free sulfur, autocatalytic oxidation is observed in a system containing 40 per cent of the original concentration of amine. The *N*-phenyl-2-naphthylamine which remains at the beginning of apparent oxygen absorption in vulcanizates shows only half the inhibiting effect of pure *N*-phenyl-2-naphthylamine on the oxidation of rubber.

5. Combined sulfur takes part in the oxidation process along with the hydrocarbon part of the vulcanizate.

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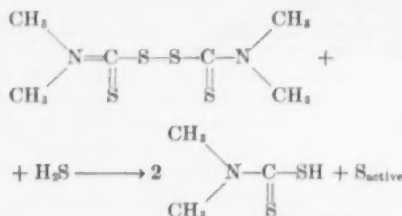
REACTION OF A THIURAM AND SULFUR *

G. A. BLOKH AND L. P. SAZONOVA

In a previous article¹ the occurrence of an intensive interchange between atoms of elemental sulfur when present as vulcanizing agent and the sulfur atoms of the mercapto group of mercaptobenzothiazole as accelerator was shown by the isotopic method, i.e., by the application of tagged atoms of radioactive sulfur. Thus, the existence of a reaction between the accelerator and the vulcanizing agent during the vulcanization of rubber was established.

The application of isotopes as tagged atoms is an effective new method of investigating the chemical structure of substances, their reactivities, and the mechanism of chemical reactions in which they take part. This method is being successfully developed in our country, particularly by the work of Brodskii and his pupils².

The present study is devoted to the problem of the reaction of tetramethylthiuram disulfide (hereafter called thiuram) and elemental sulfur. Studies in this field are of great scientific and practical interest, since the mechanism of the accelerating action of thiuram is not yet clear. We assume that the chemistry of the reaction is as follows. Thiuram is decomposed during vulcanization, with the formation of a dithiocarbamate and free active sulfur. Because of this, the thiuram can vulcanize rubber without the addition of elemental sulfur to the mixture. Such vulcanizates are particularly widely used in the cable industry.



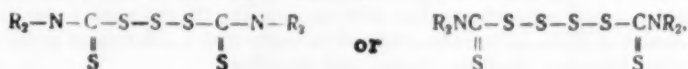
As for the hydrogen sulfide, its formation can result either from a reaction of free sulfur with the rubber, resins, or proteins, or from a reaction of the accelerator containing sulfur with the rubber or mixtures of the latter.

There are no experimental data in the scientific literature on the formation of intermediate compounds between a thiuram and sulfur. Furthermore, in comparisons of the reaction of diphenylguanidine with thiuram, a number of investigators have shown that in any explanation of the different rates of accelerating activity of diphenylguanidine and thiuram, it is necessary to consider the almost instantaneous liberation of sulfur from the latter, while the action of diphenylguanidine depends on the rate of two reactions: (1) its union with sulfur, i.e., the formation of an intermediate unstable compound, and (2) the

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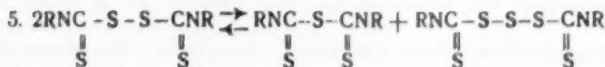
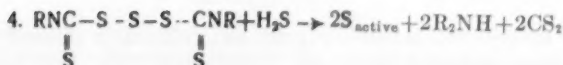
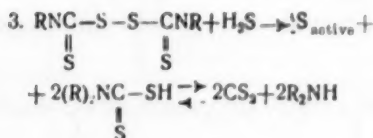
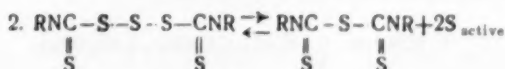
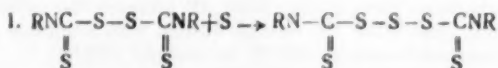
decomposition of this intermediate compound. The possibility of intermediate compounds between thiuram and sulfur has not been studied.

Criticizing the adherents of the chemical theory, Margaritov³ has called for an explanation why the time to the point when an accelerator begins to show its action is approximately the same for thiuram and diphenylguanidine. It would seem that accelerators which contain no sulfur, e.g., diphenylguanidine, should have a longer quiescent period than disulfides of the type of thiuram, if we assume that this period is spent in the formation of additional unstable polysulfides. It is perfectly evident that there is a reaction between thiuram and sulfur during vulcanization, with the formation of a number of intermediate unstable polysulfide compounds of the type:



which, when destroyed, liberate not only atomic sulfur, but also other products of the decomposition of dithiocarbamates. It then becomes clear why the induction period for a thiuram is not less than that of accelerators for which the formation of intermediate compounds is assumed.

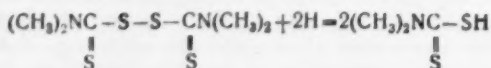
Here are examples of possible reactions:



However, a reaction between thiuram and the products of its decomposition, for example, dimethylamine, is not, of course, impossible.

The present study was undertaken in order to prove directly the occurrence of a reaction between thiuram and sulfur, using the method of tagged atoms⁴. We studied the exchange reactions between thiuram and radioactive sulfur in fusion mixtures, in solutions, and in rubber through a wide range of temperatures, i.e., 50°, 78°, 100°, 120° and 140° C for 5, 10, 15, 30, and 60 minutes and longer. The thiuram-sulfur ratio was chosen as 2:1, on the basis of the theory of the possible complete substitution of all the sulfur atoms in the thiuram structure. The method of separating the thiuram from the sulfur after the

reaction was as follows. As is already known, thiuram is a product of the oxidation of dimethylthiocarbamic acid, and can easily be transformed into the latter. The thiuram reduction reaction is:

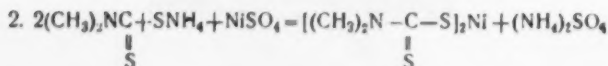
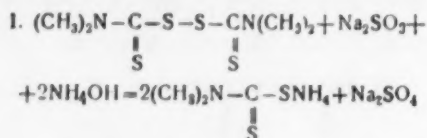


A reliable method of quantitative measurement of dithiocarbamates is also known, based on the formation of a slightly soluble nickel salt of dithiocarbamic acid⁴.

Thus, we were able to separate thiuram, in the form of nickel dithiocarbamate, from free radioactive sulfur (S^{35}) by reducing the thiuram, precipitating the dissolved dithiocarbamate obtained in water with a solution of nickel salt, and then filtrating, washing, drying, and weighing.

We used the method of determining thiuram developed by Ginzburg and Derechinskaya⁵, according to which 0.1–0.2 gram of thiuram is dissolved in 15 cc. of pure 96 per cent alcohol with very mild heating (below the boiling point). The reducing agent, consisting of 10 cc. of 10 per cent sodium sulfite and 25 cc. of 10 per cent ammonia, is added to the cooled solution. Then 10 cc. of 4 per cent aqueous nickel chloride or nickel sulfate is added to the solution. The nickel carbamate precipitates; after 10 minutes the solution is filtered through a Schott glass filter, the residue washed with ammonia and then cold water (6–7 times), and dried at 100° C to constant weight.

The chemistry of this reaction is as follows:



After the reaction between thiuram and radioactive sulfur S^{35} (according to the scheme indicated above), the thiuram and sulfur were separated, and nickel carbamate was thus obtained, the radioactivity of which was then studied.

Sodium-butadiene rubber was used in this study. The sheets were vulcanized in a press. After vulcanization, each sheet was fine-ground and then extracted with distilled water in order to remove the water-soluble products of the decomposition of thiuram, including dithiocarbamates, which were precipitated with nickel salts. The radioactivity of these salts was then determined. After the water extraction, the rubber sample was extracted with alcohol in order to extract the undestroyed part of the thiuram, reduce it, and separate it in the form of the nickel salt of the dithiocarbamate, the activity of which was then determined.

It can be clearly established from the data shown in Tables 1 and 2 that, between free sulfur and the sulfur in the thiuram structure, an intensive interchange of sulfur atoms takes place during both fusion of the two and vulcaniza-

TABLE 1

RADIOACTIVITY OF NICKEL CARBAMATE SEPARATED AFTER FUSION OF TETRAMETHYLTHIURAM DISULFIDE WITH RADIOACTIVE SULFUR (S^{35})

Time (min.)	Fusion system		Radioactivity of 1 mg. of nickel carbamate in percentage based on the meter as 100 per cent
	Temp. ($^{\circ}$ C)	Time (min.)	
1	50	120	0
2	78	120	0
3	100	10	0
4	100	15	0
5	100	25	129
6	100	30	167
7	100	60	207
8	140	10	431
9	140	30	476
10	140	60	460

tion of the rubber. This attests to the formation of intermediate compounds between sulfur and thiuram. This reaction takes place at 100° C.

It also follows from Table 2 that, during vulcanization, thiuram decomposes into a dithiocarbamate, which can be recovered from its water solution by precipitation with nickel salts. The salts indicated, being radioactive, show that

TABLE 2

RADIOACTIVITY OF NICKEL CARBAMATE SEPARATED FROM WATER EXTRACTS OF RUBBER FILMS VULCANIZED WITH TETRAMETHYLTHIURAM DISULFIDE AND RADIOACTIVE SULFUR (S^{35})

Time (min.)	Vulcanization system		Radioactivity of 1 mg. of nickel carbamate in percentage based on the meter as 100 per cent
	Temp. ($^{\circ}$ C)	Time (min.)	
1	140	15	383
2	140	60	321

an interchange of sulfur atoms takes place not only with thiuram, but also with its decomposition products formed during vulcanization.

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STUDIES OF THE MECHANISM OF THE MASTICATION OF RUBBER. VIII. THE REACTION OF NATURAL RUBBER WITH 3,5-DIBROMOBENZOYL PEROXIDE *

MINORU IMOTO AND SHIGERU KIRIYAMA

INTRODUCTION

Recently Delalande¹ found that the *p*-bromobenzoxy group can be introduced into the rubber molecule by the action of *p*-bromobenzoyl peroxide.

We synthesized 3,5-dibromobenzoyl peroxide and studied its reaction in a natural-rubber solution. Rubber was recovered from the solution, and its molecular weight and bromine content were determined. The viscosity-lowering of the solution was also observed.

EXPERIMENTAL

SYNTHESIS OF 3,5-DIBROMOBENZOYL PEROXIDE

3,5-Dibromobenzoyl peroxide (hereafter termed DBPO) was synthesized from *p*-nitrotoluene by standard procedures. The yield was 75 per cent, the melting point 167.5° C, and the bromine content 56.84 per cent (calculated value 57.11).

REACTION OF RUBBER SOLUTION WITH DBPO

A half liter of 0.5 per cent rubber solution in benzene was placed in a round-bottomed flask and immersed in a thermostat at 45° C. After reaching a definite temperature, 1.2290 grams of DBPO (corresponding to 0.06 mole per isoprene unit) was added and the mixture was shaken for five minutes. After the DBPO had dissolved, the flask was kept at this temperature.

After 4 hours, the reaction mixture was removed to a beaker and 500 cc. of methanol was added, with stirring, to precipitate the degraded rubber. The precipitate, after removal of the upper layer by decantation, was passed by a glass rod in order to squeeze out the solvent. If the above procedure was not performed quickly, unreacted DBPO stuck to the precipitated rubber (DBPO is insoluble in methanol). The free DBPO in the sample could be completely removed by repeating the process four times. The sample obtained was dried at 120° C for three hours. The intrinsic viscosity of a rubber solution in benzene was determined in a thermostat at 25° C ($\pm 0.02^\circ$) and the molecular weight was calculated by the following equation:

$$[\eta] = 5.02 \times 10^{-4} \times M^{0.667}$$

$[\eta]$ was obtained by changing the concentration of the rubber solution, as in Figure 1.

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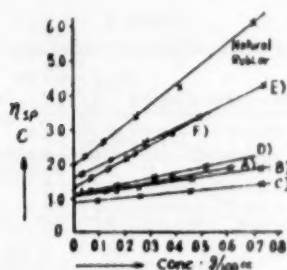


FIG. 1.—Determination of $[\eta]$ of natural and the degraded rubbers.

MEASUREMENT OF VISCOSITY LOWERING

Viscosity lowering of a rubber solution was observed under conditions of various molar ratios of DBPO per isoprene unit at 60°, 55°, 50°, 45°, and 41° C, respectively.

Twenty cc. of a rubber solution was placed in the viscometer, then a definite quantity of DBPO was added, and the whole was shaken for three minutes to dissolve the reagent. The viscosity of the solution was observed at definite time intervals.

RESULTS

The contents of combined bromine in the samples were determined, and are shown in Table 1. In this Table, A to F express the conditions of reaction, as follows:

- A. In air.
- B. With bubbling of air.
- C. In the absence of air, and with furfurylamine, a promotor, in the molar ratio of $\text{NH}_2/\text{DBPO} = 3/1$.
- D. With bubbling of nitrogen.
- E. In an atmosphere of nitrogen, which was introduced by replacing five times the evacuated air with nitrogen gas.
- F. In an atmosphere of nitrogen, as in E, but also with addition of tetrahydrofurfurylamine (molar ratio of $\text{NH}_2/\text{DBPO} = 3/1$).

In the conditions of D, E, and F, the solvent, benzene, was distilled in nitrogen.

The number N of the 3,5-dibromobenzoxy groups attached to one molecule of rubber are listed in the lowest line of Table 3. The N values can be calculated from the value of the bromine contents and the molecular weights. In this calculation, it was assumed that the following decomposition had not occurred.



In the cases E and F, it was impossible to obtain accurate values, because the combined bromine contents were too small.

In Table 1, it is clear that, in the absence of air, the values of N were only 0.6–3.2. But in the presence of air or oxygen, the value of N rose to 4.9–16.8. In the cases of E and F, we may assume that M is nearly equal to 1.

TABLE 1

(The molecular weight of natural rubber used was 250,000.)

Sample	In the presence of oxygen					In the nitrogen atmosphere				
	A		B		C	D		E		F
Condition of reaction	In air		Bubbling of air		In air, <chem>-CH2-</chem> <chem>NH2</chem>	Bubbling of nitrogen		In nitrogen		In nitrogen, with tetrahydrofurfurylamine
Number of times of reprecipitation	4	5	4	5	4	4	5	4	5	4
Br content (%)	2.78	2.59	1.68	1.68	0.67	0.67	0.66	0.69	—	0.068
Average Br content (%)	2.69		1.68		0.72	0.67		0.069		0.067
Molecular weight	100,000		100,000		100,000	77,400		185,000		144,500
<i>N</i> *	16.8		10.5		4.9	3.2		0.8		0.6

* *N* is the number of benzoxy groups per molecule of rubber. The values of the molecular weights described above are the viscosity-average and not the number-average. Accordingly, the values of *N* are inexact. But it may be informative to know the round values and to compare them.

The results of the observations on the viscosity lowering of the rubber solution are shown in Figures 2 and 3, which represent only two examples of many experiments.

ATTEMPT TO DETERMINE THE REACTION ORDER

From the results shown in Figure 2, several parallel lines, as shown in Figure 4, could be drawn, and Figure 4 shows the relations of time *t* required to reach a definite η value and concentration of DBPO. From the slope of these lines, the order of the reaction may be deduced.

First, the following relationship can be introduced in cases when excess rubber was used:

$$v = k[\text{C}_6\text{H}_6]^m[\text{DBPO}]^n = k'[\text{DBPO}]^n \quad (1)$$

where v_n is the velocity of the reaction and *k* is a constant. The velocity *v* can be expressed by:

$$v = k'' \cdot v_n = k''' \times (1/t) \quad (2)$$

where v_n is the velocity of the viscosity lowering and *t* is the time required to reach a definite η_{rel} value.

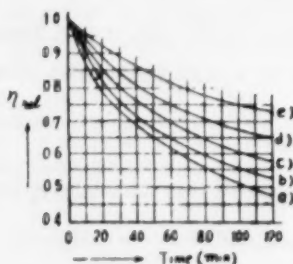


Fig. 2.—Viscosity lowering of a natural rubber solution by DBPO, changing the molar ratio of DBPO/C₆H₆

- a) DBPO/C₆H₆ = 0.1
- b) = 0.03
- c) = 0.06
- d) = 0.04
- e) = 0.02

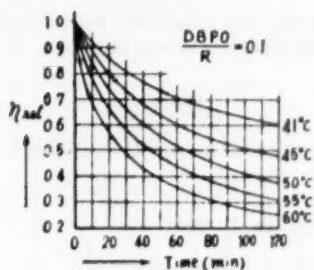


FIG. 3.—Viscosity lowering of a natural rubber solution by DBPO at several temperatures, where DBPO/C₅H₈ is constant.

Then:

$$\log (1/t) = K + n \cdot \log [\text{DBPO}] \quad \left(K = \log \frac{k''}{k'''} \right)$$

From the slopes of the lines in Figure 4 the order of the reaction of DBPO, the value of n could be calculated. It was found to be 0.77.

Figure 5 shows the relation between the logarithm of the reciprocal of the time required to reach a certain η value and the reciprocal of absolute temperature.

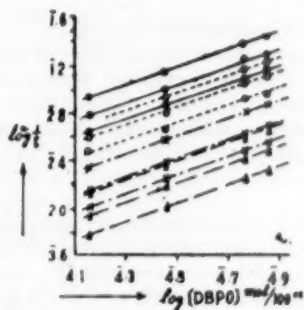


FIG. 4.—Relation of time required to reach a definite η and concentration of DBPO.

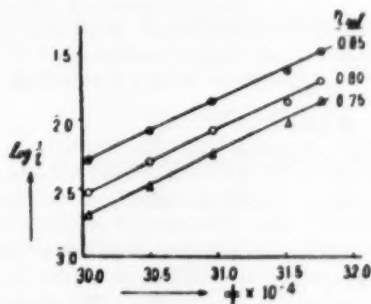
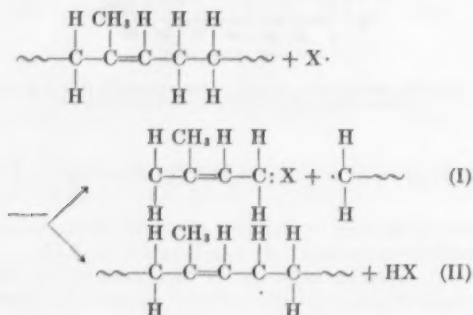


FIG. 5.—Relation of time and temperature.

ture. The activation energy was calculated from the slope of the lines in this figure. An E value of 20,600 calories was obtained.

DISCUSSION

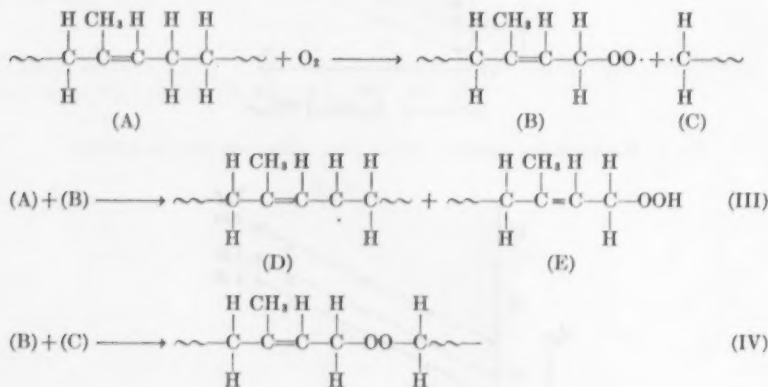
As described in the previous paper², the radical $X\cdot$ can act on a rubber molecule in two ways, as follows:



Here $X\cdot$ is oxygen or a fragment of the DBPO.

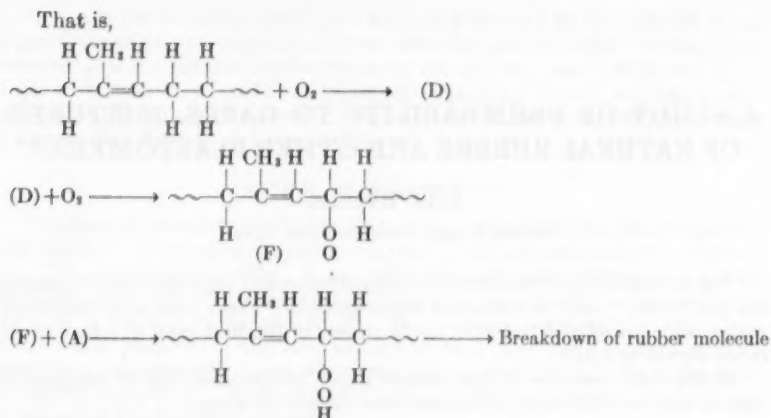
Let us discuss the mechanism of the reaction of the rubber molecule with DBPO in the presence or absence of oxygen. Four probable reactions may be considered.

Class 1.— $X\cdot$ is O_2 and the reaction is (I). In this case the reaction may be shown schematically as follows:

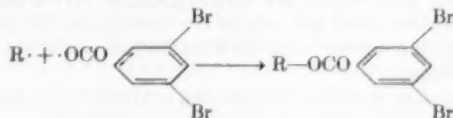


In reaction (III), the rubber molecule is broken down. The radical (D) will be discussed in Class 2.

Class 2.— $X\cdot$ is O_2 and the reaction is (II). The reaction belonging to this class has been treated by Farmer and coworkers.



The breakdown of the rubber molecule proceeds in this way. The above-mentioned rubber radicals R· may combine, not only with each other, but also with radical fragments of DBPO as follows.



Class 3.—X· is $\text{Br}_2\text{C}_6\text{H}_3\text{COO} \cdot$ and the reaction is (I). In this case the rubber molecule breaks down immediately, as described by us².

Class 4.—X· is $\text{Br}_2\text{C}_6\text{H}_3\text{COO}$ and the reaction is (II). The rubber radical (D) produced can react with oxygen or a DBPO fragment in accord with the scheme of Class 2.

From this classification, some conclusions may be drawn. As shown in Table 1, the bromine content of degraded rubber, i.e., the value of *N*, was larger in air than in nitrogen. This may be caused by the reaction of Class 2.

The breakdown of the rubber molecule proceeded more easily in air than in nitrogen, as interpreted from the molecular weight values. This result shows that the reaction of Class 2 is important for the breakdown of the rubber molecule, as described by many authors.

But also, the decrease of the molecular weight was observed in nitrogen. In this case, it may be recognized clearly that an immediate breakdown of the rubber chain by the benzoxy radical occurred.

SUMMARY

The reaction of a natural-rubber solution with 3,5-dibromobenzoyl peroxide was carried out, and the following results were obtained.

1. Lowering of the viscosity of the rubber solution was observed.
2. Bromine contents in the degraded rubber were determined.
3. The molecular weight of the degraded rubber was determined.

The reaction of rubber with DBPO is discussed on the basis of these observations.

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A STUDY OF PERMEABILITY TO GASES. MIXTURES OF NATURAL RUBBER AND OTHER ELASTOMERS *

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The permeability of elastomeric high polymers has been the subject, during the last twenty years, of numerous investigations¹, which have been concerned with a wide variety of technical applications, in the first rank of which inner tubes should be cited.

In the work described in the present paper, the permeability of mixtures of natural rubber with other elastomers was chosen for study.

PERMEABILITY MEASUREMENTS

It is already known that, in the passage of a gas through a rubberlike membrane, several phenomena are distinguishable: (1) solution of the gas molecules in the rubber from one side of the membrane; (2) diffusion of these molecules through the rubber; and (3) evaporation of the gas from the other side of the membrane.

The solution and evaporation phenomena conform to the law of Henri:

$$C = h \cdot P \quad (1)$$

which expresses the proportionality between the concentration C of the gas in the rubber phase and the pressure P . The factor h is the solubility coefficient.

The diffusion conforms to the law of Fick:

$$\frac{dC}{dt} = D \left(\frac{\partial^2 x}{\partial^2 C} + \frac{\partial^2 C}{dy^2} + \frac{\partial^2 C}{dz^2} \right) \quad (2)$$

which expresses the concentration C at the instant t by a point on the coordinates x , y , and z , when the diffusion coefficient D is known.

By applying Equations (1) and (2) to the simple case of a membrane of uniform thickness when a condition of permanent passage of gas has been established, there is derived the equation:

$$q = D \cdot h \cdot A \cdot t \cdot \Delta P \cdot \frac{1}{d} \quad (3)$$

where q is the quantity of gas that has passed through the membrane, A is the area of the membrane, t is the time, ΔP is the difference of pressure between the two surfaces, and d is the thickness of the membrane.

If A , r , ΔP , and d are unity, the simple relation is obtained:

$$Q = D \cdot h \quad (4)$$

a relation which defines the permeability coefficient Q .

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Revue Générale du Caoutchouc*, Vol. 31, No. 5, pages 393-396, May 1954.

Here h is the solubility coefficient, which is expressed by the number of cc. of gas (converted to normal conditions) dissolved per cc. under 1 atmosphere pressure; D is the diffusion coefficient in sq. cm. per sec., and P is the no. of cc. of gas (converted to normal conditions) which pass, per second, through a rubber sample having a surface area of 1 sq. cm. and thickness of 1 cm., as a result of a pressure difference of 1 atmosphere.

METHOD OF MEASUREMENT

The method adopted was that of Barrer² and applied by van Amerongen³ in later studies. This method recommends itself by its precision and reproducibility. The principle is simple. A gas cell is divided into two parts by a thin membrane of the rubber to be tested. The gas is made to enter, at atmospheric pressure, at one side of the membrane. The increase of pressure per unit time in the other chamber of the cell, which has been previously evacuated, is a function of the quantity of gas which has been passed through the membrane during the same time. From this, the permeability coefficient Q is calculated by means of the following equation:

$$Q = \frac{\Delta P}{\Delta t} \cdot \frac{V}{P} \cdot \frac{d}{A} \cdot \frac{273}{T} \quad (5)$$

where ΔP is the increase of pressure in time Δt ; V is the volume of the apparatus on the side of low pressure; P is the pressure of the gas on the side of entrance into the membrane; d is the thickness of the membrane, and T is the absolute temperature.

The assembly of the apparatus is shown schematically in Figure 1.

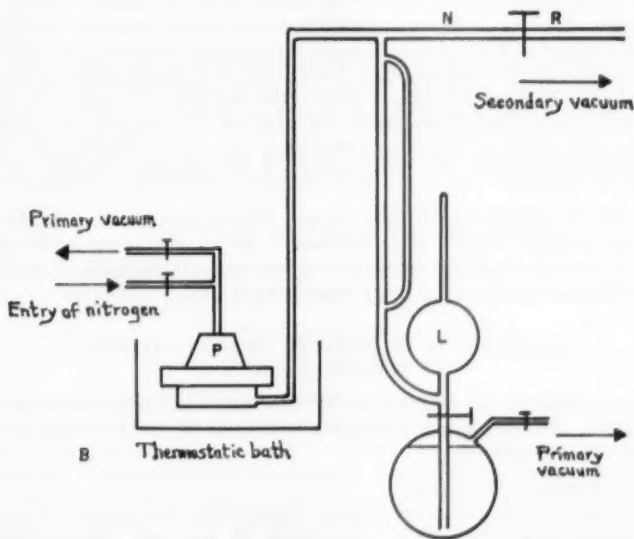


FIG. 1.—Schematic diagram of the apparatus for measuring permeability. P—Cell of the permeameter; N—Glass connection; L—MacLeod gauge; R—Stopcock valve.

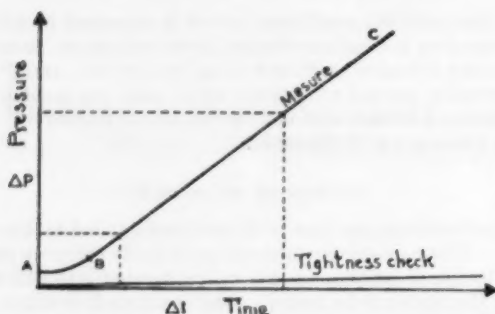


Fig. 2.—Pressure differential on the two sides of a membrane as a function of the time.

The pressure measurements were made by means of a MacLeod gauge.

After degassing the system for the purpose of eliminating gases occluded in the apparatus and in the membrane, the tightness of the connections was ascertained by checking the pressure at regular intervals. Nitrogen was then admitted into the upper chamber of the cell of the permeameter. Starting at this instant, recordings made at short intervals by means of the MacLeod gauge were utilized to construct curves of the difference of pressure on the two sides of the membrane as a function of time. This relation is shown diagrammatically in Figure 2.

The curve in Figure 2 is comprised of two sections: (1) AB, representing a transitory condition, i.e., the establishment of a concentration gradient through the membrane, and (2) BC, representing a permanent condition. From the slope of the straight line BC, the $\Delta P/\Delta t$ value can be calculated directly.

The permeability is an exponential function, which increases rapidly with the temperature³. With this parameter maintained constant, the influence of various factors on the permeability coefficients of natural-rubber vulcanizates was studied. Neither the time of milling nor the time of vulcanization have, within wide limits, any considerable influence on the permeability coefficient. The molecular weight of a synthetic elastomer above the relatively low range of 3000 has no influence on the permeability of compounded mixtures of elastomers.

A series of measurements of a chosen vulcanizate, made with the same membrane, showed that the error inherent in the apparatus can be accepted as negligible; in most cases the error in measurements attributable to the apparatus may be considered as not more than 3–4 per cent.

PERMEABILITY TO NITROGEN OF SOME MIXTURES OF VARIOUS ELASTOMERS

The permeability to nitrogen at 60° C of unloaded mixtures based on natural rubber and containing different proportions of the following synthetic elastomers was measured.

Polyisobutylene (Vistanex).

Butadiene-acrylonitrile copolymers (Paracril-26, containing 18 per cent acrylonitrile; Paracril-35, containing 26 per cent acrylonitrile; and

Hycar OR-15, containing above 42 per cent acrylonitrile).

Polychloroprene (Neoprene Type W)

Chloroprene-acrylonitrile copolymer (Neoprene Type Q).
Organic polysulfide (Thiokol-FA)
Hycar PA-21
Vulcaprene
Nitrilex

In these experiments, the operating technique was first to prepare two masterbatches.

(1) A masterbatch of the particular elastomer containing the proper vulcanizing agents.

(2) A masterbatch of natural rubber, the accelerator system of which was compatible with the synthetic rubber with which the masterbatch was to be blended, particularly with respect to similar optimum times of vulcanization.

From these masterbatches, mixtures of different pairs of elastomers were prepared by blending on a mill proportions of the elastomers such that mixtures containing 20, 40, 60, and 80 parts, respectively, of the particular elastomer per 100 parts of total elastomer were obtained.

NOTES

Vistanex is chemically saturated and cannot be vulcanized. Butyl rubber, which contains 1-2 per cent of copolymerized isoprene, and can be vulcanized, was chosen as representative of the polyisobutylene type of elastomer. Thiokol-FA is extremely difficult to vulcanize when it is not loaded. In elastomer mixtures containing more than 40 parts of Thiokol-FA, no success was had in obtaining membranes free of serious defects. Hycar PA-21, Vulcaprene, and Nitrilox were not tested in the form of natural-rubber blends.

EXPERIMENTAL RESULTS

In all cases the permeability coefficients found experimentally have been based on the coefficients, measured under the same conditions, of the base mixture of natural rubber, A, to which the permeability coefficient 100 was arbitrarily assigned.

In order to indicate the order of magnitude, the absolute value of the permeability coefficient for nitrogen at 60° C of this A mixture is recorded as follows:

$$Q = 31.5 \times 10^{-8} \text{ cc./sq. cm./s./atm.}$$

The experimental results are summarized in Table 1.

Let V represent the synthetic-elastomer content of the mixture:

$$V = \frac{\text{Weight of synthetic elastomer}}{\text{Weight of natural rubber} + \text{synthetic elastomer}}$$

In Figure 3, curves (I) record, as good examples, the decrease of permeability with increase of the proportion of Vistanex and of Paracril. All the curves show a more or less pronounced concavity, in all cases toward the positive ordinates. This shows that the decrease of permeability is always greater than it would be if it were directly proportional to the content of synthetic elastomer. Expressed differently, the decrease of permeability does not depend solely on the permeability of the particular synthetic elastomer itself. For example, it was found that, although Vistanex and Neoprene Type Q have almost the same permeabilities themselves, their effects on the permeability of natural rubber are

TABLE I
PERMEABILITY COEFFICIENTS OF NATURAL RUBBER-SYNTHETIC ELASTOMER MIXTURES CONTAINING VARIOUS PROPORTIONS OF THE TWO

Synthetic -rubber component	Parts of synthetic elastomer per 100 parts of total elastomer					
	0	20	40	60	80	100
Vistanex	100	63	42	—	—	4.4
Paracril-26	100	77	58	44	30	25
Paracril-35	100	78	54	34	16	11.5
Hycar OR-15	100	63	57	22.5	—	6
Neoprene-W	100	77	63	44	30.4	21.5
Neoprene-Q	100	53	—	21.5	—	4.2
Thiokol-FA	100	86	50	—	—	—
Hycar PA-21	100	—	—	—	—	9.5
Vulcoprene	100	—	—	—	—	9
Nitrilex	100	—	—	—	—	45

distinctly different: e.g., 20 parts of Neoprene Type Q reduces the permeability of natural rubber more than does the same proportion of Vistanex (see Table I).

REPRESENTATION OF THE SPECIFIC IMPERMEABILIZING POWER
OF THE SYNTHETIC ELASTOMERS STUDIED

Let it be assumed that, instead of being dispersed in each other, the two elastomers form two distinct layers of uniform thickness, the thickness of each layer being proportional to the content of elastomer. The "equivalent" permeability coefficient of the mixture as expressed theoretically and verified experimentally by van Amerongen⁴ is:

$$\frac{1}{Q_c} = \frac{1-V}{Q_1} + \frac{V}{Q_2} \quad (6)$$

where Q_c is the equivalent permeability coefficient, V is the content of the component with permeability Q_2 , and $1-V$ is the content of the component with permeability Q_1 . This relation expresses the additivity of the impermeabilities ($1/Q$) of the two components.

If, for each of the elastomers which were studied as mixtures with natural rubber, the relative values of the permeability coefficient Q_A which would correspond to the proportionality between the impermeabilizing effect and the V value, the relative values of the experimental coefficient Q_B , and the relative values of the equivalent coefficient, Q_C , of the two superposed layers of elasto-

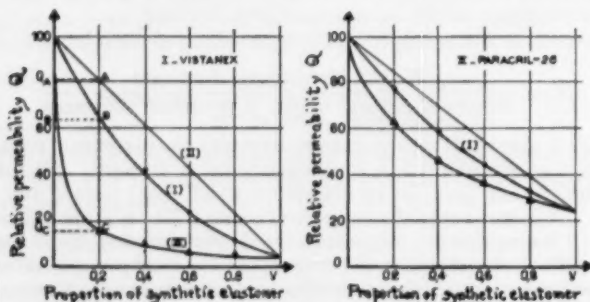


FIG. 3.—Permeability coefficients, Q_A , Q_B , and Q_C , at 60° C, of natural rubber-synthetic elastomer mixtures as a function of their content, V , of synthetic elastomer.

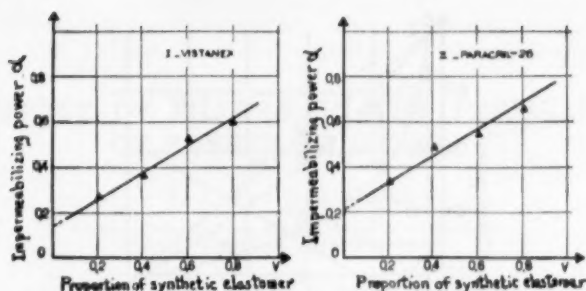


Fig. 4.—Impermeabilizing power α of two synthetic rubbers as a function of their content V in mixtures with natural rubber.

mers are expressed as functions of V , then the curves (I), (II), and (III) of Figure 3 are obtained.

Let α be the ratio AB/AC (see Figure 3), or, expressed otherwise:

$$\alpha = \frac{Q_A - Q_B}{Q_A - Q_C} \quad (7)$$

and plot for each elastomer the calculated values of the coefficient α as a function of V , as shown in Figure 4.

Figure 4 shows: (1) that α depends both on the particular elastomer and on the proportion V of the elastomer in the mixture; (2) that the relation of α to V is linear for all the elastomers, and the higher is the V value, the more closely does the reduction of permeability approach the effect observed by van Amerongen, and (3) that the straight lines which, for the various synthetic elastomers studied, represent this relation are parallel to one another, and have slopes which are practically the same, i.e., approximately 0.6.

The results obtained with Vistanex and with Paracril are cited merely as examples. The foregoing remarks apply likewise to all the other synthetic elastomers studied, and so satisfactorily that one is justified in drawing certain definite conclusions.

The first logical conclusion to be drawn from the experiments is that the impermeabilizing power of any synthetic elastomer in blends with natural rubber can be characterized by the ordinate with origin α_0 of the straight line representing α as a function of V . The approximate α_0 values recorded in Table 2 were found.

Knowing the relative permeability coefficient of a synthetic elastomer and the coefficient of a mixture containing V_0 parts of this elastomer with natural rubber, the permeability coefficient of a mixture containing V parts of this same synthetic elastomer can be derived by constructing a simple geometric diagram, the principle of which is shown in Figure 5.

TABLE 2

Synthetic elastomer	α_0
Paracril-35 NS-90	0.05
Neoprene-W	0.12
Vistanex	0.15
Hycar OR-5	0.20
Paracril-26 NS-90	0.22
Neoprene-Q	0.27

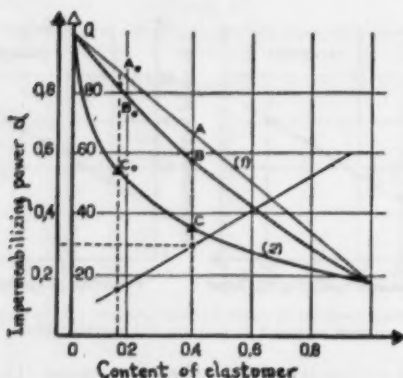


Fig. 5.—Determination of the permeability coefficient Q_B of a mixture containing V parts of synthetic elastomer, when the coefficient Q_0 of a mixture containing V_0 parts of the same elastomer is known.

The proportionality straight line (1) in Figure 5 for Q_A and curve (2) are constructed, calculating Q_C for different values of V by means of Equation (6). The relation: $\alpha_0 = A_0 B_0 / (A_0 C_0)$ is then derived, and through the point $\alpha_0 - V_0$ a straight line is drawn, having slope 0.6, whose ordinate at V on the abscissa gives α . It is then necessary only to divide the section AC into the relation: $AB/AC = \alpha$ to read directly the permeability coefficient Q_B of the mixture V .

CONCLUSIONS

An investigation of the permeability to nitrogen of various mixtures of natural rubber and synthetic elastomers has brought to light one highly important fact. The lower permeability obtained by the addition of a synthetic elastomer does not depend solely on the permeability coefficient itself of the particular synthetic elastomer. Rather, it depends in addition on another factor, which, in all probability, is a function of the internal structure of the mixture of natural rubber and synthetic elastomer.

A study of this structure is not a simple problem, and mention is made only of the fact that, after having attempted unsuccessfully to analyze the structure by classic methods of microscopy, very encouraging results have been obtained with mixtures of natural rubber and Paracril-26 by measuring, at radio frequencies, the loss factor.

The results indicate that, at least with natural rubber-Paracril-26 mixtures, milling brings about a certain degree of mutual diffusion of the two elastomers on a molecular scale. However, the vulcanizates give indications of a two-phase colloidal structure, one phase relatively rich in Paracril, the other phase relatively rich in natural rubber. Such a structure would be in harmony, at least qualitatively, with the conclusions drawn in the present investigation on the permeability to gases of mixtures of elastomers.

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THE EFFECT OF FILLERS ON THE PERMEABILITY OF RUBBER TO GASES *

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There are two ways of increasing the impermeability of rubber products to gases. One method, which has been of great success, is the development of new types of synthetic rubber. Figure 1 shows that Neoprene, for example, is only about one-sixth as permeable to air as is natural rubber. Butyl rubber has become an outstanding material for the manufacture of inner tubes. The impermeability of Butyl rubber is 10 to 20 times that of natural rubber, depending on the temperature.

Another means of changing the permeability of rubber is the addition of fillers. Very little has so far appeared in the literature regarding the effect of fillers on the permeability of rubber to gases. Davey and Ohyo¹ obtained vari-

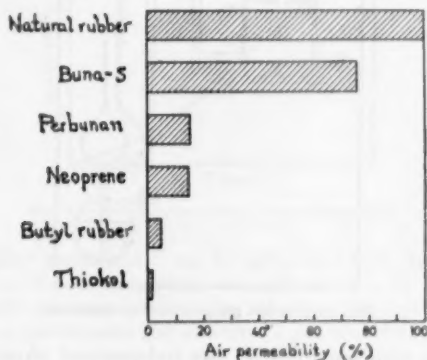


Fig. 1.—Permeability of different types of rubber to air at 25° C

able and unreliable data on rubber mixtures containing 10 per cent of carbon black, zinc oxide, aluminum oxide, and whiting. Morris², however, observed a decrease of permeability of natural rubber up to 31 per cent with 15 volume-per cent of the same fillers. Some measurements of permeability to hydrogen have also showed a reducing effect by fillers³. A greatly decreased permeability to gases was observed with rubber mixtures containing powdered aluminum or mica as fillers⁴.

The purpose of the work to be described was to study in greater detail the effect of fillers on the permeability of natural rubber to gases. It seemed of

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from *Kautschuk und Gummi*, Vol. 7, No. 6, pages WT 132-136, June 1954. This paper was presented at the meeting of the German Rubber Society at Goslar, May 7-9, 1953.

particular interest to obtain data on the influence of various carbon blacks and some of the new light-colored reinforcing fillers.

METHOD OF MEASUREMENT

Figure 2 shows the apparatus with which the permeability was measured⁶. A rubber diaphragm reinforced with gauze separates the gas chamber A from the evacuated chamber B. The pressure in chamber B is measured with a MacLeod manometer, with a range up to 1.5 mm. mercury and accuracy of 0.001 mm. mercury.

In order to derive a characteristic material constant, it is necessary to have some idea of the process of permeation. All previously known facts accord with the view that, in the process of permeation, the gas dissolves in the rubber as in an ordinary liquid, and then diffuses to a region of lower concentration, where the gas can again evaporate.

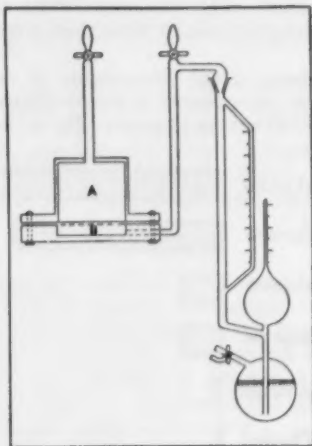


FIG. 2.—Vacuum gas permeability apparatus.

Permeation is thus governed by two independent physical processes: (1) the solubility of the gas, and (2) the diffusion of the gas inside the rubber. For these processes, Henry's law and the first law of Fick can be applied:

$$C = S \cdot p \quad (1)$$

and

$$q = D \cdot A \cdot t(C_1 - C_2)/d \quad (2)$$

Combination of (1) and (2) gives:

$$q = Q \cdot A \cdot t(p_1 - p_2)/d \quad (3)$$

In these equations, q denotes the amount of gas penetrating through the rubber, calculated from the increase of pressure, volume, and temperature of the vacuum chamber; D is the diffusion coefficient or the diffusivity; S is the solubility coefficient; C_1 and C_2 are the concentrations of gas in the surface of the diaphragm; p_1 and p_2 are the equilibrium gas pressures in the gas chamber, which

in the measurements described were in most cases 1 atmosphere and maximal 1.5 mm. Hg; A is the effective surface area of the diaphragm (here 30.2 sq. cm.); d is the thickness of the diaphragm (0.3 to 1.0 mm.); and t is the time.

The new coefficient Q , which is usually called the permeation coefficient or the permeability, is an important one. This coefficient, which indicates the quantity of gas which permeates under standard conditions, is related to the solubility coefficient and diffusion coefficient by the following simple equation:

$$Q = D \quad (4)$$

The diffusion coefficient can be derived⁶ by means of the following equation:

$$D = d^2 \quad (5)$$

This equation, which was derived by Daynes⁷ from the general law of diffusion (second law of Fick), gives the diffusion coefficient D as a function of the induction time θ . This time is determined by extrapolating the increase of pressure time curve after reaching a state of permeation in a previously completely evacuated membrane on the zero axis, as illustrated in Figure 3. It can be shown mathematically that permeation equilibrium (Point B) is only reached after a period three times as long as the induction⁸ period θ .

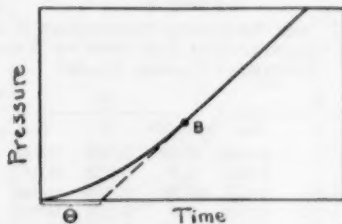


FIG. 3.—The induction period θ in gas permeation.

The gas solubility coefficient S can be calculated very simply by means of Equation (4) from the permeability and diffusivity. In addition, several direct measurements were made with a special apparatus previously described⁸, determining with a gas burette the amount of gas absorbed by finely divided rubber.

Hereafter Q will be expressed in cc. of gas at 0° C, and 760 mm. mercury pressure, which penetrates a membrane 1 sq. cm. and 1 cm. thick in 1 second at a pressure difference of 1 atmosphere; D in sq. cm. per second; and S in cc. of gas at 0° C, and 760 mm. mercury pressure, which is dissolved in 1 cc. of material at 1 atmosphere pressure of gas.

The diaphragm was prepared in the usual way by the dry procedure, i.e., after mixing, the rubber was pressed out to a thin diaphragm during vulcanization. In a few cases, the rubber was calendered to a thin sheet before vulcanization. The thickness of the diaphragm was measured by a Schopper thickness gauge, with an accuracy of about 0.01 mm.

INFLUENCE OF CARBON BLACK

Tables 1 and 2 show the effect of carbon black on the permeability, diffusivity, and solubility of some gases in natural-rubber mixtures of the following

TABLE 1
PERMEABILITY Q TO GASES OF RUBBER MIXTURES CONTAINING 50
PER CENT BY WEIGHT OF DIFFERENT CARBON BLACKS

	H_2		N_2		O_2		CO_2	
	25° C	50° C	25° C	50° C	25° C	50° C	25° C	50° C
Thermax (MT)	30×10^{-3}	72×10^{-3}	4.6×10^{-3}	15.0×10^{-3}	13.2×10^{-3}	36.5×10^{-3}		
P 33 (FT)	29.5	73	4.6	15.0	13.0	36.5		
Statex K (VFF)	27.5	68	4.2	14.0	12.1	34		
Vulcan 3 (HAF)	27	67	4.0	13.5	11.2	32.5	47×10^{-3}	124×10^{-3}
Spheron 9 (EPC)	28.5	69	4.2	13.9	12.1	34		
Spheron 4 (HPC)	31	76	4.1	13.8	12.3	35	59	147
No filler	38	93	6.4	21	18	49	101	221

composition: smoked sheet 100, zinc oxide 5, sulfur 2, stearic acid 1, Santocure 1, and carbon black 50; these mixtures were vulcanized 20 minutes at 142° C.

The solubility was in a few cases determined not only indirectly from the permeability and diffusivity, but also more precisely by direct gas absorption measurements. The results of both measurements agree on the whole within the limits of experimental accuracy. It is, of course, necessary to evacuate the rubber containing active carbon blacks very thoroughly at elevated temperatures in order to obtain reproducible data.

TABLE 2
DIFFUSION COEFFICIENT D AND SOLUBILITY COEFFICIENT S OF GASES IN RUBBER
MIXTURES CONTAINING 50 PER CENT BY WEIGHT OF
DIFFERENT CARBON BLACKS

	Temp. ° C	H_2			N_2			O_2		
		$D \times 10^6$	S	$S_{av.}$	$D \times 10^6$	S	$S_{av.}$	$D \times 10^6$	S	$S_{av.}$
Thermax	25			0.036	0.96	0.048	0.048	1.4	0.094	0.088
	50			0.041	2.9	0.052	0.047	3.8	0.096	0.090
P 33	25	7.2	0.041	0.038	0.96	0.048	0.048	1.4	0.093	0.098
	50	17	0.043	0.042	2.9	0.052	0.048	3.8	0.096	0.092
Statex K	25	2.8	0.098	0.11	0.53	0.079	0.097	0.64	0.19	0.19
	50	7.3	0.093	0.099	1.7	0.082	0.097	2.2	0.15	0.16
Vulcan 3	25	2.0	0.13	0.12	0.50	0.080	0.15	0.54	0.21	0.35
	50	5.2	0.13	0.09	1.7	0.079	0.11	1.8	0.18	0.25
Spheron 9	25	2.5	0.11	0.13	0.11	0.38	0.46	0.19	0.64	0.61
	50			0.12	0.52	0.27	0.28	0.75	0.45	0.41
Spheron 4	25	1.9	0.16	0.13	0.10	0.41	0.61	0.15	0.82	0.93
	50	5.6	0.14	0.11	0.35	0.39	0.42	0.58	0.60	0.58
No filler	25	10.0	0.038		1.1	0.058		1.65	0.109	
	50	22	0.042		3.5	0.060		4.8	0.102	

Differences in the permeability of various gases through the same diaphragm can be explained by considering the influence of the nature of the gas on its rate of diffusion and on its solubility. A gas with relatively small molecules has a relatively high rate of diffusion, and a gas with a high boiling point has a relatively high solubility in rubber⁸.

What is noteworthy in Table 1, however, is that, although very great differences were observed in the solubility and diffusivity of the same gas as functions of the type of carbon black, the permeability is practically independent of the type of carbon black and is about 70 per cent of that of the corresponding unloaded rubber mixture. Any increase observed in the solubility of a particular gas appears to be connected with a corresponding decrease of its diffusivity. To explain this remarkable phenomenon, let us first consider the

solubility factor. If the solubility data obtained by the direct method, e.g., for oxygen, are shown as a function of some characteristic property of the particular carbon black, Figure 4 is obtained. It is seen that the solubility of oxygen increases sharply, if a fine active carbon black is added to the rubber. The specific surface areas were determined by nitrogen adsorption on the carbon blacks at a low temperature (-196°C).⁹ Evidently a part of this well known capacity of carbon black for adsorbing gases is retained after the carbon black is incorporated into rubber. One must conclude, then, that the adsorptive capacity of carbon black is only to a partial degree nullified by any rubber present. It is easy to conceive that small capillaries and cavities in the carbon black particles which are not filled with rubber molecules can still adsorb gaseous molecules.

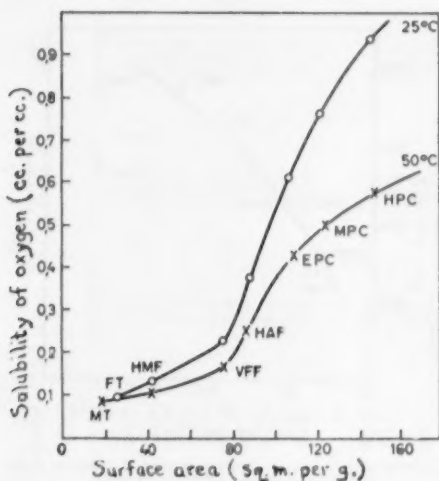


Fig. 4.—Solubility of oxygen in rubber mixtures containing carbon blacks of different specific surface areas.

The solubility value of a gas, as obtained experimentally, is therefore a combination of its normal solubility in rubber and a frequently large degree of adsorption of the gas on carbon black. Since the permeability, as shown in Table 1, is independent of this adsorption of gas, it may be concluded that the gas adsorbed on the carbon black is not involved in the actual permeation process itself.

The low diffusivity which is observed in cases where the solubility of a gas is high can also be explained as an adsorption of a part of the gas on the carbon black, provided that it is assumed that the adsorbed gas no longer takes part in the diffusion process. The diffusivity value obtained in this way gives a mean value of the diffusivity of a gas diffused under normal conditions in rubber and that of the gas which has been rendered inactive by being adsorbed on the carbon black.

It should be mentioned that here Equation (5) is based on a linear decrease of the concentration of gas in the diaphragm. A nonlinear dependence of the

gas absorption by carbon black in rubber on the concentration of the gas would lead to deviations in the measurements of diffusivity.

It is interesting that a high gas solubility resulting from adsorption of the gas on carbon black can have a great influence in the oxidation of rubber, in contrast to the effects involved in permeation.

Figure 5 shows the rates of oxidation of some rubber-carbon black mixtures, which were also used in the experiments recorded in Table 1, in relation to the solubility of oxygen. This rate of oxidation was determined by direct volumetric gas measurements of the amount of oxygen irreversibly adsorbed by 1 gram of finely divided rubber at 1 atmosphere pressure at 80° C. A high solubility of oxygen is thus reflected in a high rate of oxidation, which in turn will have an unfavorable effect on aging.

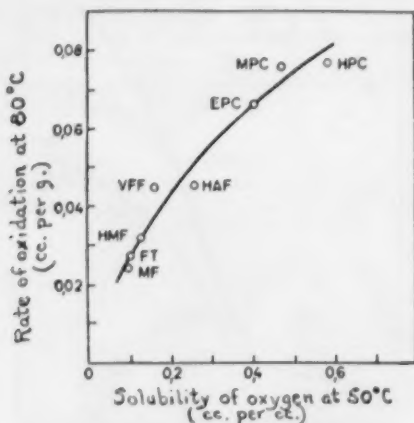


FIG. 5.—Rate of oxidation of rubber-carbon black mixtures at 80° C in relation to the gas solubility at 50° C.

EFFECT OF ORDINARY LIGHT COLORED FILLERS

Tables 3 and 4 (Section A) show measurements of natural rubber containing a number of ordinary inorganic fillers, including some light-colored reinforcing fillers, such as aluminum hydroxide, aluminum silicate, and calcium silicate types. No marked specific effects were observed. In general, then, the reduction by 20 parts by volume of filler per 100 parts of rubber of the permeability of oxygen, nitrogen, and hydrogen is about 25 per cent, regardless of the particular filler. Bentone¹⁰, an organic bentonite, gives a similar result when mixed with rubber latex.

Figure 6 shows that the permeability of rubber to gases decreases slowly but steadily with increase of the filler content. The behavior of Durosil can be regarded as typical of the other ordinary fillers listed in Section A of Table 3. The observed decrease of permeability and diffusivity can be readily explained by the longer path which the gas molecules must travel through the rubber in order to circuit the impermeable particles of filler. The diaphragm thus behaves like another thicker diaphragm containing no filler.

TABLE 3
PERMEABILITY Q TO GASES OF RUBBER MIXTURES CONTAINING 20 PER CENT BY VOLUME OF DIFFERENT LIGHT COLORED FILLERS

Filler	% by weight Mixture	H ₂		N ₂		O ₂		CO ₂	
		25° C	50° C	25° C	50° C	25° C	50° C	25° C	50° C
A. Ordinary fillers									
Whiting	58	I	31×10 ⁻⁸	74×10 ⁻⁸	4.8×10 ⁻⁸	15.7×10 ⁻⁸	13.6×10 ⁻⁸	37×10 ⁻⁸	
Iron oxide	112	I	29	71	4.7	15.0	13.2	36	
Aluminum oxide	52	I	32	79	5.1	16.8	14.5	40	
Barium sulfate	95	I	31	75	4.9	15.8	13.8	38	
Bentone	60	II	28	71	4.3	14.6	12.4	35	
Hi-Sil	57	II	25	61	3.8	12.3	11.1	31	
Cal-Sil	42	II	32	79	5.1	16.8	14.0	41	
Durosil	45	II	28	70	4.4	14.5	11.7	35	44×10 ⁻⁸
Aerosil	48	III	28	68	4.2	13.7	11.8	33	98×10 ⁻⁸
Teg-N	46	II	30	73	4.8	15.7	13.7	38	57
Sileg-AS7	47	II	32	78	4.7	16.2	14.0	40	129
Ultrasilteg VN3S	50	III	27	66	3.6	13.0	10.9	32.5	
B. Lamellar fillers									
Alumina	58	I	12.6	30.5	2.0	6.4	5.4	15	19
Mica	62	I	8.4	20.5	1.3	4.3	3.6	10.3	13
Graphite	52	I	20	49	3.1	10.1	8.8	24.5	29
Bentonite	56	II	12	30	1.9	6.3	5.3	15	23
No filler		I	38	93	6.4	21	18	49	101
									221

Mixtures I, II, and III contained 20 parts by volume of filler. Mixtures I and II were vulcanized 20 min. at 149° C; Mixture III 30 min. at 149° C. The base mixtures were (in parts by weight) as follows: Mixture I; rubber, 100 sulfur 2, phenyl-2-naphthylamine 1, stearic acid 1, Santocure 1, zinc oxide 5. Mixture II; rubber 100, sulfur 2.5, phenyl-2-naphthylamine 1, stearic acid 2, Santocure 1, zinc oxide 5. Mixture III; rubber 100, sulfur 3, phenyl-2-naphthylamine 1, stearic acid 3, Santocure 3, zinc oxide 5.

TABLE 4
DIFFUSION COEFFICIENT D AND SOLUBILITY COEFFICIENT S OF GASES IN RUBBER MIXTURES CONTAINING 20 PER CENT BY VOLUME OF DIFFERENT FILLERS

Filler	Temp. °C	H ₂		N ₂		O ₂	
		$D \times 10^6$	S	$D \times 10^6$	S	$D \times 10^6$	S
A. Ordinary fillers							
Whiting	25			0.95	0.051	1.4	0.097
	50			2.8	0.056	3.6	0.103
Aluminum oxide	25			1.0	0.051	1.5	0.097
	50			2.9	0.058	3.9	0.103
Barium sulfate	25			0.94	0.052	1.4	0.099
	50			2.8	0.056	3.7	0.103
Hi-Sil	25	4.1	0.061	0.63	0.060	0.62	0.18
	50	10.3	0.059	1.9	0.065	1.7	0.18
Durosil	25	4.4	0.064	0.88	0.050	0.90	0.13
	50	11	0.063	2.8	0.053	2.5	0.14
Aerosil	25	6.2	0.045	0.76	0.055	1.2	0.098
	50	13	0.052	2.5	0.055	3.2	0.103
Teg-N	25	7.0	0.043	0.86	0.056	1.2	0.11
	50	15	0.049	2.5	0.063	3.2	0.12
B. Lamellar fillers							
Aluminum	25	3.9	0.032	0.40	0.050	0.57	0.095
	50	8.2	0.037	1.25	0.051	1.5	0.010
Mica	25	2.7	0.031	0.30	0.043	0.42	0.086
	50	5.5	0.037	0.88	0.049	1.15	0.089
No filler	25	10.0	0.038	1.1	0.058	1.65	0.109
	50	22	0.042	3.5	0.060	4.8	0.102

As with carbon black, it is possible that a part of the gas is inactivated by being adsorbed on the filler. In comparison with rubber mixtures containing reinforcing carbon blacks, mixtures containing light-colored reinforcing fillers show, in general, lower oxygen solubility. The rate of oxidation and the aging of these mixtures will, therefore, probably be better than for rubber-carbon black mixtures.

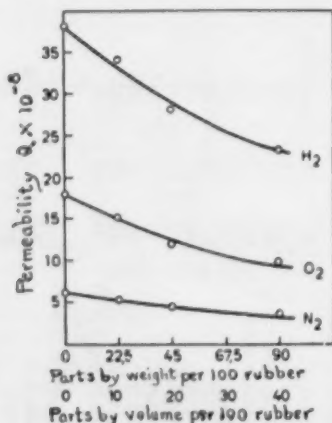


FIG. 6.—Permeability of rubber mixtures at 25° C containing increasing loads of Durosil.

EFFECT OF LAMELLAR FILLERS

Section B of Figure 3 shows a relatively large decrease of permeability for a number of natural rubber-filler mixtures, while Section B of Table 4 gives some corresponding diffusivity and solubility data. The best result is for a mixture containing 20 parts by volume of powdered mica per 100 parts of rubber; this mixture shows only 22 per cent of the permeability of the corresponding unloaded rubber mixture. Figure 7 gives the permeability of this mixture, compared with that of unloaded rubber and Butyl rubber. At 25° C, the differences between this and Butyl rubber are still considerable, but the differences decrease rapidly with rise of temperature. At 100° C, the permeability of the natural rubber-mica mixture is practically the same as that of Butyl rubber. The relatively strong reducing effect of the fillers listed in Table 3, Section B, on the permeability is probably explainable by the lamellar nature of the particles of all these fillers⁴. With powdered mica, this lamellar structure is related to the crystalline structure, as in the case of graphite. In bentonite (colloidal

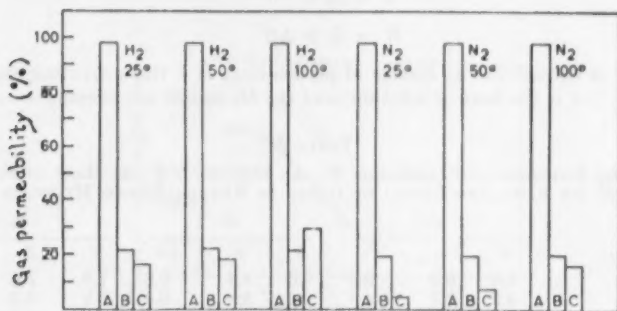


Fig. 7.—Gas permeability of a natural rubber-mica mixture in comparison with unloaded natural rubber and Butyl rubber.

A Pure-gum natural rubber.
 B Natural rubber containing 20 vol.-% mica.
 C Butyl rubber.

alumina), the effect is observed only when, after treatment in aqueous suspension with hydrochloric acid, this filler is mixed with latex, and the latex mixture is then dried and a diaphragm prepared from it in the usual way. It is known that bentonite in aqueous suspension may disintegrate into individual lamellar particles¹¹. It has also been reported in the literature that particles of aluminum powder may be as much as 25 times as long as they are thick, and that paint films containing aluminum powder show a low permeability¹².

It may be assumed that lamellar fillers have a much greater mechanical obstructing effect on the diffusion of gas molecules than do normal isotropic filler particles, because the gas molecules must travel a longer path to pass around the filler particles. Perhaps this obstruction to the diffusion of gas is increased by a certain orientation of the filler particles. Powdered aluminum particles have, for example, the property of forming tile-like layers in paint films¹³. The same effect should appear in rubber diaphragms. At any rate it is probable that the filler particles are oriented at the surface of the diaphragm during calendaring or pressing in manufacturing operations¹⁴. Evidence of an orientation anisotropy was revealed by measurements of swelling.

The elongation of a diaphragm containing powdered mica, caused by swelling in benzene, was 45 per cent parallel to the surface, but 80 per cent perpendicular to this direction⁴.

It is of importance to use the finest fillers possible. Ordinary commercial grades of lamellar fillers are relatively coarse, and this has an unfavorable effect on the tear resistance and residual elongation of the rubber.

TEMPERATURE DEPENDENCE

One obtains an insight into the energy relations during the permeation process by a consideration of its dependence on the temperature. It is known¹⁵ that this temperature relation can be described, in first approximation, by the following equations:

$$Q = Q_0 \cdot e^{-W/(RT)} \quad (6)$$

$$D = D_0 \cdot e^{-E/(RT)} \quad (7)$$

$$S = S_0 \cdot e^{-\Delta H/(RT)} \quad (8)$$

$$W = E + \Delta H \quad (9)$$

where W is the activating energy of permeation, E is the activating energy of diffusion, ΔH is the heat of solution, and Q_0 , D_0 and S_0 are constants.

TABLE 5
ACTIVATING ENERGIES OF PERMEATION W AND DIFFUSION E AND HEAT OF SOLUTION ΔH (IN KCAL. PER MOLE) OF GASES IN RUBBER-FILLER MIXTURES

Filler	H_2			N_2			O_2		
	W	E	ΔH	W	E	ΔH	W	E	ΔH
P-33	6.9	6.6	0.3	9.0	8.4	0.6	7.9	7.6	0.3
Statex-K	6.9	7.3	-0.4	9.2	8.9	0.3	7.9	9.4	-1.5
Spheron-4	6.9	8.3	-1.4	9.3	9.7	-0.4	8.0	10.3	-2.3
Whiting	6.7			9.1	8.3	0.8	7.6	7.2	0.4
Aluminum oxide	6.8			9.1	8.1	1.0	7.8	7.3	0.5
Barium sulfate	6.8			9.0	8.4	0.6	7.8	7.4	0.4
Hi-Sil	6.8	7.1	-0.3	8.9	8.4	0.5	7.8	7.7	0.1
Durosil	7.0	7.0	0.0	9.1	8.9	0.2	8.4	7.8	0.6
Aerosil	6.8	5.6	1.2	9.1	9.1	0.0	7.9	7.5	0.4
Teg-N	6.8	5.8	1.0	9.1	8.2	0.9	7.8	7.5	0.3
Aluminum	6.8	5.7	1.1	8.9	8.7	0.2	7.8	7.4	0.4
Mica	6.8	5.4	1.4	9.1	8.2	0.9	8.0	7.7	0.3
No filler	6.8	6.0	0.8	9.1	8.8	0.3	7.6	8.1	-0.5

Table 5 summarizes the various energy values, calculated by Equations (6), (7), and (9). It is noteworthy that the activating energy of permeation of any particular gas is practically independent of the presence of a filler in the rubber mixture. This fact is a convincing proof of the assumption that the permeation process itself is not, on the basis of energy, influenced by the filler. Differences in the permeability observed for a particular gas are, therefore, of purely mechanical nature, and bear no relation to the energy factors. To be sure, considerable differences are found in the activating energy of diffusion and the heat of solution of rubber-carbon black mixtures. Figure 8 shows, however, that the heat of solution, calculated directly from the measurement of oxygen solubility, depends to a large degree on the specific surface area of the particular carbon black. Evidently this "heat of solution" consists of the true

heat of solution of the gas in the rubber and the heat of adsorption of the gas on the carbon black. This heat of adsorption is, because of the experimental method, also included in the activating energy of diffusion. It is, consequently, useless to attempt to draw further conclusions from the value of the latter energy factor.

SUMMARY

The purpose of the investigation was to study the effects of fillers, especially various types of carbon black and new light-colored reinforcing fillers. In the discussion of the problem, it is shown that permeability to gases is related to the rate of diffusion, and to the solubility of the gas in rubber, and it is also shown how these properties were measured.

The effect of carbon black on the permeability of rubber to gases is relatively small. Independent of the type of carbon black, the permeability is reduced only about 30 per cent by the addition of 50 parts by weight of carbon black per

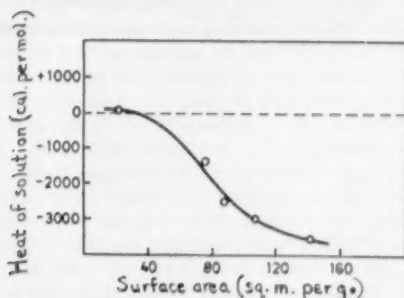


Fig. 8.—Heat of solution of oxygen in natural rubber-carbon black mixtures in relation to the specific surface area of the carbon black.

100 parts of rubber. The permeability of a rubber mixture to a gas is increased considerably, however, by the presence of fine types of carbon blacks, while the rate of diffusion of the gas is decreased. This fact can be explained by assuming that gas is adsorbed by carbon black in rubber and thereby rendered inactive. The high oxygen adsorption of the finer types of carbon blacks in rubber mixtures explains the high rate of oxidation of such mixtures.

A whole series of inorganic fillers, among them some light-colored reinforcing agents, have no noteworthy effect on permeability. With 20 parts by volume of such fillers per 100 parts of rubber, the permeability is decreased only about 25 per cent, irrespective of the particular filler.

A considerable decrease of permeability, i.e., about 75 per cent, is observed, however, with lamellar fillers, such as powdered aluminum and powdered mica. A rubber mixture containing powdered mica shows, at 100° C, the same permeability to hydrogen and nitrogen that Butyl rubber does.

The relation of permeability to the temperature of rubber containing fillers is practically the same as that for an unloaded rubber mixture. The decreases of permeability to gases which are observed, are, therefore, not related to energy factors, but are of a purely mechanical nature.

ACKNOWLEDGMENT

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IMPORTANCE OF THE POLAR COMPONENT OF MIXED FLUIDS IN THE SWELLING OF VULCANIZATES *

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The problem of the relation of the swelling of vulcanizates to the nature of the liquid medium is very important in explaining the nature of vulcanization and determining the nature of the bond between the separate macromolecules in the vulcanizate. The relation of the swelling of vulcanizates to the molecular polarization of mixed liquids has been studied several times¹; however, the mechanism of the reaction of the polar component of a mixed liquid with the rubber molecules during swelling is still not very clear. According to contemporary theory², the swelling of polymers, particularly rubber, is thermodynamically analogous to the mixing of low-molecular liquids. Swelling is caused by a decrease of the free energy of the system: $\Delta G = \Delta H - T \cdot \Delta S$, which in the case of nonpolar polymers is due principally to an increase of entropy, $T \cdot \Delta S$, as a result of the separation of the molecular chains and their increased elasticity. For polar polymers, ΔH is the important factor.

In this work rubber is regarded as a polymer in which the molecular chains are bound by nonequivalent bonds with varying amounts of energy, as appears in the swelling process, and not as a union of molecular chains surrounded by a uniformly strong field³. It is evident from other studies⁴ that the latter assumption is not entirely correct. On the basis of a study of the protective action of antioxidants during the oxidation of rubber by oxygen, one of the authors⁵ regarded the mechanism of this action as the result of solvation of the antioxidant in the polar segments of the rubber molecule by the polar molecules.

In this case an attempt was made to explain the mechanism of reaction of the polar components of the liquid with the rubber molecules according to swelling data. The swelling of vulcanizates in various mixed liquids was studied. The composition of the rubbers and the vulcanization conditions are shown in Table 1.

The components of the liquids, chemically pure substances, were carefully purified by the usual methods. The degree of swelling was determined gravimetrically. The reproducibility of the swelling experiments was about 1.5 per cent. The swelling of unextracted rubbers was studied in order not to change their properties. For the experiments on distribution, which were made with an interferometer, the rubbers were carefully washed in benzene, ethyl alcohol, and alcohol-benzene mixtures until extraction was complete, with interferometric control. Swelling was measured after 48, 72, 120, and 168 hours. In each case the kinetic curves were drawn, and the degree of swelling was determined from them.

The binary mixtures studied can be divided into 2 groups.

1. The first group of liquids consists of binary systems of nonpolar and weakly polar substances: benzene-*p*-dichlorobenzene (Figure 1, (1)), benzene-

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Doklady Akademii Nauk SSSR*, Vol. 80, No. 3, pages 505-508 (1953).

TABLE I
COMPOSITIONS AND PROPERTIES OF THREE VULCANIZATES

	I	II	III
Natural rubber	100	100	100
Sulfur	4	2.75	2.75
Free	0.96	0.65	0.64
Combined	3.04	2.10	2.11
Zinc oxide	25.	5.	5.0
Stearic acid	1.	1.	1.
Mercaptobenzothiazole	1.25	0.85	0.85
Carbon black	35.	—	40.
Rubberax	—	—	5.
Aldol	1.	—	—
Whiting	50.	58.8	—
Paraffin oil	—	2.	—
Pitch	2.	—	—
Vulcanization time (minutes)	30	20	20
Vulcanization temperature (° C)	143	143	143
Modulus (50%) (kg. per sq. cm.)	—	68	115
Tensile strength (kg. per sq. cm.)	—	163	147
Relative elongation (%)	—	645	580
Residual elongation (%)	—	18.7	29

p-dinitrobenzene (similar curve), benzene-chlorobenzene (Figure 1 (2)), benzene-toluene (Figure 2 (3)), chloroform-ethyl ether (Figure 2 (2)). In all these systems, an increase of concentration of the liquid which is largely responsible for swelling causes a uniform steady increase of the degree of swelling.

2. The second group consists of systems of nonpolar and strongly polar substances or substances with a reactive functional group (type of hydrogen bond): benzene-aniline (Figure 1 (3)); benzene-*p*-dinitrobenzene (similar curve); benzene-nitrobenzene (Figure 1 (4) and Figure 2(1)), benzene-*p*-nitrochlorobenzene (similar curve). For all these systems, a maximum is observed on the degree of swelling vs. concentration curves in the range of low concentrations of the polar component, and a steeper descent of the curve at higher concentrations of the polar component. For vulcanized rubber of the same composition (Figure 1 (3 and 4)), the position of the maximum on the concentration axis is to a large degree independent of the nature of the polar component of the liquid mixture.

The data obtained can be interpreted as follows. The rubber chains contain, besides the nonpolar and weakly polar (double bonds) segments, relatively strongly polar groups (chiefly oxidized oxygen-containing substances), which react in part with one another by means of hydrogen bonds, and in part remain free. Consequently, as a result of the movement of the molecular chains, a static equilibrium is achieved between the chains bound to similar chains and the free polar groups. The bonds between the chains of the rubber high polymer are thus caused by hydrogen bonds, as well as by van der Waals forces.

In vulcanizates, along with the sulfur bridges, the polar bonds facilitate the formation of the system⁶. During swelling, as a result of the separation of the molecular chains, equilibrium between the bound and free polar groups is displaced toward an increase of the free groups. Small quantities of a polar component in a binary fluid mixture facilitate this process by screening the polar groups of the rubber. Larger quantities of the polar component greatly reduce the elasticity of the molecular chains, and, consequently, the degree of swelling.

The free polar groups are able to react with the molecules of the polar component of a binary mixture. When the concentration of the polar component is less than the proportion of polar groups in the rubber, there is a prevailing attraction of the polar component into the rubber phase, in comparison with the nonpolar component. The result is a greater activity of the polar component in the rubber phase than in the solution, and, consequently, an additional attraction of the nonpolar component into the rubber phase. At higher concentrations of the polar component in a binary mixture, the reverse relations are observed; the activity of the polar component in the solution is greater than in the rubber phase, and this causes isolation of the nonpolar component and, therefore, a decrease of the degree of swelling. It should be remembered that the position of the maximum is determined by the optimum reaction between rubber and liquid. In order to confirm these assumptions, we measured the equilibrium relations of the amount of the polar component to the amount of the nonpolar component in the rubber phase and in the solution during swelling in an ethyl alcohol-benzene system, and observed the prevailing attraction of the alcohol into the rubber phase at low alcohol concentrations in the solution, and the prevailing attraction of benzene at high alcohol concentrations in a binary mixture.

It is known⁷ that the molecular weight of rubbers, measured in polar fluids, is less than in nonpolar fluids. We observed an increase of solubility of rubber in a nonpolar solvent in the presence of small quantities of a polar component. The maximum solubility was observed⁸ for hexane with the addition of alcohols and ketones.

Sokolov and Feldman⁹ observed a sharp change in the order of mechanical properties of polymers after small equimolar additions of various plasticizers. These phenomena are due to the fact that the polar molecules of the fluid

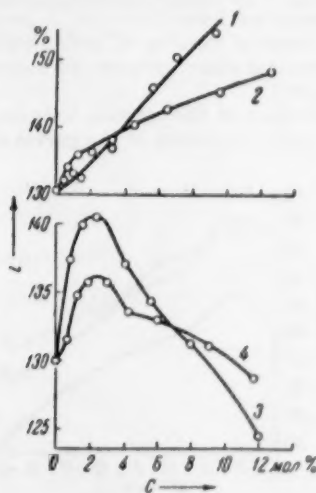


FIG. 1.—Swelling of rubber. Curve 1.—Benzene-*p*-dichlorobenzene. Curve 2.—Benzene-chlorobenzene. Curve 3.—Benzene-aniline. Curve 4.—Benzene-nitrobenzene.

The abscissa indicates the mole-per cent concentration, *C*.

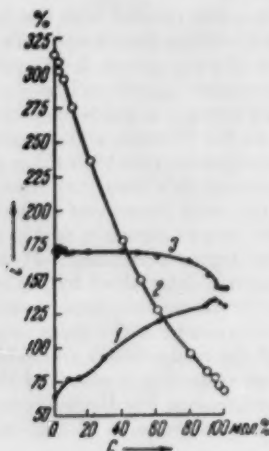


FIG. 2.—Swelling of rubber. Curve 1.—Benzene-nitrobenzene. Curve 2.—Ethyl ether-chloroform. Curve 3.—Benzene-toluene.
The abscissa indicates the mole-per cent concentration, C.

facilitate rupture of the polymer chains on the bonds formed by the polar groups.

A study of the swelling of rubbers of varying composition in a benzene-aniline system showed that the position of the maximum depends on the properties of the polymer (see Figure 3). As for the height of the maximum, it seems to be related to the energy of reaction of the polar groups in the rubber and the polar components of binary mixtures.

The course of the degree of swelling vs. concentration curves in benzene-nitrobenzene and chloroform-ether systems were determined by physical-chemical analysis (Figure 2).

The influence on swelling of the reaction between the components of a binary fluid is seen from a comparison of the curves shown with the heat of

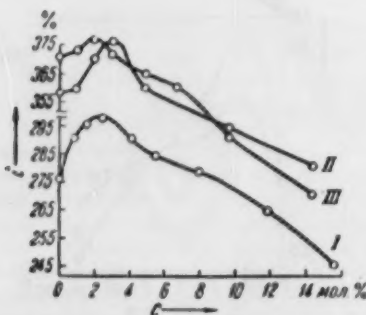


FIG. 3.—Swelling of vulcanizates I, II, and III, in the benzene-aniline system. The degree of swelling was calculated as the percentage of liquid absorbed by weight of rubber in each vulcanizate.
The abscissa indicates the mole-per cent concentration, C.

mixing-concentration curves or the molar heat capacity-concentration curves¹⁰. For certain systems, such deviations from an additive curve, caused by the reaction of components of binary mixtures, can lead to the appearance of maxima and minima³ (chloroform-butyl acetate and hexane-ethyl acetate systems). However, the nature of these maxima and minima depends essentially on the reaction of the components of the binary mixtures, while the nature of the maxima on the swelling curves studied here, as has already been shown, is basically the result of the reaction between the polar groups of the rubber and the polar component of the mixed fluid. For swelling, the essential factor is not the analytical concentration of the polar component in the binary fluid, but the concentration of unassociated separate molecules, which are only absorbed by the polar groups of the polymer, as has been shown in a number of investigations¹¹. The course of the swelling curves is determined by the complex reaction of the components of the fluid with each other and with the polymer. From this viewpoint, such a system is triple, and the polymer can influence the other components of the mixture, for example, by releasing part of the associated components.

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THERMODYNAMICS OF THE SWELLING OF NATURAL RUBBER AND SODIUM-BUTADIENE RUBBER IN BINARY MIXTURES *

G. L. STAROBINETS AND KH. M. ALEKSANDROVICH

The thermodynamics of ternary systems containing high polymers has been developed only in recent years. In a number of studies¹, the thermodynamic functions of systems of high polymers and two low-molecular liquids have been calculated. On the other hand, the experimental determination of the thermodynamic functions of the high polymer phase has not been considered in studies of swelling in binary fluids². At present, almost the only criterion of the validity of theories of the thermodynamics of swelling in binary fluids is the applicability of the theory in predicting the degree of swelling. Data with which it is possible to determine to what extent any theory can predict the distribution of low-molecular components in both phases are very sparse³, and there are hardly any data which indicate the accuracy of theoretical calculations of the free energy, heat content, and entropy factors.

Evidently a strict theory of the thermodynamics of ternary systems of high polymers must be based on reliable experimental data. We admit that, in the present work, an undesirable gap exists between the experimental study of the thermodynamics of ternary systems with high polymers and the theoretical treatment of this problem.

The partial molar thermodynamic functions, viz., free energy, heat content, and entropy, of low-molecular components in systems of vulcanized natural rubber, benzene, and lower alcohols, and systems of vulcanized sodium-butadiene rubber, benzene, and lower alcohols (from methyl to butyl inclusively), in equilibrium with binary solutions have been studied in this work.

EXPERIMENTAL PART

Swelling was studied in 100-cc. flasks with ground stoppers furnished with glass hooks to suspend the specimens in the saturated vapors; the stoppers of the flasks were lubricated with graphite.

The same volume of solution, viz., 10 cc., and approximately the same weight of rubber of standard dimensions were chosen for the experiments. In other respects the experimental method, including preliminary rinsing of the rubber and interferometric analysis of the composition of the solution in the polymer phase is the same as that described in earlier works⁴.

The experiments described here were carried out at 20° and 50° C. An air oven with double walls and a contact thermometer from a Hepler thermostat was used as thermostat, and a relay and electric lamp as heater. The temperature fluctuations did not exceed $\pm 0.5^\circ$ at 20° and $\pm 1^\circ$ at 50° C. Since, on the basis of our experiments, the temperature coefficient of change of the molar proportion of alcohol in the polymer phase dN^*_2/dT did not exceed 0.002, the

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accuracy of analysis of the composition was about 5 per cent. This accuracy is quite sufficient, since the transition from the activity of the components of a binary equilibrium solution to the activity of the components in the polymer phase, with the method chosen for this experiment, based exclusively on the curve of equilibrium between the polymer and binary solution. The flasks containing the specimens were carefully blackened.

The swelling of vulcanized natural rubber of the following composition was studied: rubber 100, stearic acid 1, Neozone-D 1, mercaptobenzothiazole 1.5, zinc oxide 5, sulfur 2; and a vulcanized sodium-butadiene rubber (plasticity-35) of the following composition: rubber 100, mercaptobenzothiazole 0.25, diphenylguanidine 2, zinc oxide 2, stearic acid 1, machine oil 23, oleic acid 0.5, rosin 0.5, lampblack 120, and sulfur 2.5. The natural rubber was vulcanized in a hydraulic press at 100 atmospheres' pressure and 132° C for 50 minutes,

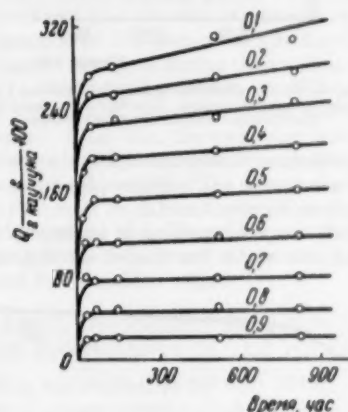


Fig. 1.—Kinetic curves of the butadiene rubber-benzene-methyl alcohol system. The figures on the curves denote the values of N_2 .

The ordinate indicates $Q = \frac{g.}{g. \text{ rubber}} \times 100$

The abscissa indicates the time in hours.

and the butadiene rubber was vulcanized in a steam vulcanizer at 4 atmospheres' pressure and 130° C for 15 minutes.

The swelling isochromes were studied in all the systems, including interferometric analysis of the composition of the solution in the polymer phase in the time interval from 30 to 2000 hours. In Figures 1 and 2, the results of such a study are presented, as examples, in the form of graphs of the degree of swelling vs. time and the molar fraction of alcohol in the polymer phase (N_2)-time (t) for a butadiene-benzene-methyl alcohol system.

It is seen from Figure 1 that the second, slow state of swelling is particularly evident in dilute alcohol solutions. Figure 2 shows that, in the first stage of swelling, the molar fraction of alcohol in the polymer phase increases with time, and in the second stage it becomes practically independent of the time. The equilibrium values of swelling were obtained, in accordance with Scott², by extrapolating to zero time the linear sections of the swelling curves corresponding to the slow stage. The degrees of swelling obtained are shown in Section 3

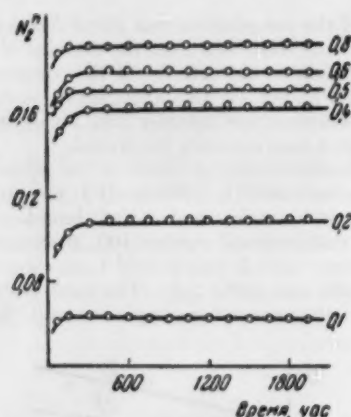


FIG. 2.—The curves of the molar fraction of alcohol in the polymer phase (N_2) vs. time for a butadiene rubber-benzene-methyl alcohol system. The figures represent the values of N_2 . The abscissa indicates the time in hours.

of Table 1. These equilibrium values correspond to the period during which the composition of the solution in the polymer phase becomes constant. This is easily seen by comparing Figures 1 and 2.

Inasmuch as the slow stage of swelling is accompanied by oxidative destruction of the polymer, the molar fraction of alcohol in the polymer phase

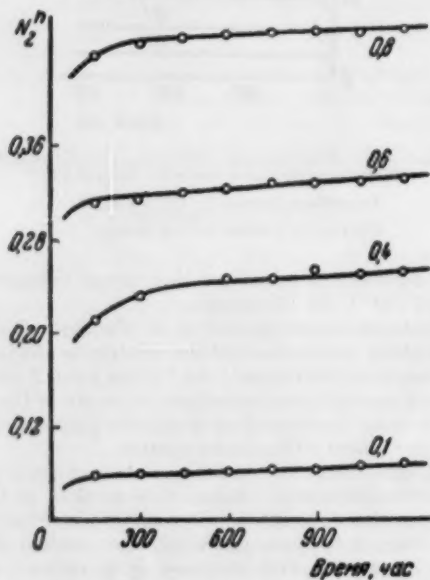


FIG. 3.—Curves of the molar fraction of alcohol in the polymer phase vs. time for the system: natural rubber-benzene-butyl alcohol. The figures on the curves denote the values of N_2 . The abscissa indicates the time in hours.

should increase slowly, owing to the increase of polarity of the polymer. This increase of the molar fraction of alcohol with time in the polymer phase is actually observed in vulcanized natural rubber; this is illustrated in Figure 3, where the curves of the molar fraction of alcohol in the polymer phase (N_2^a)—time (t) for a natural rubber-benzene-*n*-butyl alcohol system are shown.

Since the increase of the molar fraction of alcohol in the polymer phase with time indicates an increase of polarity of the polymer, the data shown in Figure 3 are experimental confirmation of the fact that the slow stage of swelling is accompanied by oxidative destruction.

No slow increase of the molecular fraction of alcohol in the polymer phase with time was observed during the swelling of sodium-butadiene rubber. This is explained, on the one hand, by the lower molecular weight of sodium-butadiene rubber, and, on the other hand, by the fact that the double bonds of the 1,2-structure in the side chains are less active with oxidizing agents⁴. The work of Dogadkin⁷ has shown that the rate of destructive solution of butadiene polymers is a linear function of the content of 1,4-structure in the polymer.

The much slower rate of oxidation during the swelling of vulcanized sodium-butadiene rubber can be illustrated by the results of the experiments described below. Specimens of natural and butadiene rubber were swollen for 14 days in saturated benzene vapor. After this, the specimens were brought to constant weight in a vacuum desiccator, then subjected to repeated swelling for 14 days, and again brought to constant weight. The increase over the original weight of vulcanized natural rubber in 28 days, calculated on the basis of 1 gram, was 0.0095 gram and of a vulcanized butadiene rubber, 0.0015 gram. The increase of the degree of swelling in the second two weeks was 6.6 per cent for natural rubber and 0.3 per cent for butadiene rubber.

VALUES OF THE PARTIAL THERMODYNAMIC FUNCTIONS OF THE LOW-MOLECULAR COMPONENTS IN THE POLYMER PHASE

Equilibrium swelling was studied at 20° and 50° C. The corrected activities of the components of binary benzene-alcohol-mixtures were calculated from the cryoscopic data and the heats of dilution by means of known thermodynamic equations. The method of the calculations has been described⁸. The reactivity values obtained for alcohols were then converted so that their values were equated to unity for pure alcohols. Thus the pure components were selected as standard states for both components of the binary mixtures. When the reactivities are standardized in this way, their values for the same component are uniform in all corresponding phases.

The reactivities of the low-molecular components in the polymer phase in relation to the composition of a swollen polymer were obtained from the curves of the composition of the solution in the polymer phase and the composition of the equilibrium binary solution. The partial molar-free energies of the components in the polymer phase were calculated from the equations:

$$\Delta \bar{F}_1 = RT \cdot \ln a_1 \quad (1)$$

$$\Delta \bar{F}_2 = RT \cdot \ln a_2 \quad (1a)$$

The average values of the partial molar heat content of the low-molecular components in the temperature range of 20–50° C were obtained by integrating the equations:

$$\frac{d(\Delta F/T)}{dt} = -\frac{\Delta H}{T^2} \quad (2)$$

TABLE 1*
VALUES OF THERMODYNAMIC FUNCTIONS OF LOW-MOLECULAR COMPONENTS IN THE HIGH-POLYMER PHASE

N ₁ Solution 1	N ₂ Polymer 2	Q mole. g. rubber 3	Q ₁ mole. g. rubber 4	Q ₂ mole. g. rubber 5	$-\Delta F_1^{\circ}$ cal. g.-mol. 6	$-\Delta F_2^{\circ}$ cal. g.-mol. 7	$\Delta \bar{H}_1$ g.-mol. 8	$-\Delta F_1^{\circ}$ cal. g.-mol. 9	$-\Delta F_2^{\circ}$ cal. g.-mol. 10	$\Delta \bar{H}_2$ cal. g.-mol. 11	$\Delta \bar{S}_1$ degree. g.-mol. 12	$\Delta \bar{S}_2$ degree. g.-mol. 13
NATURAL RUBBER-BENZENE-METHYL ALCOHOL												
0.0	0.0	3274	—	—	—	—	—	—	—	—	—	—
0.020	0.024	3661	3633	28.4	8	10	4	480	780	1500	0.045	5.74
0.040	0.045	3637	3591	45.9	15	18	8	375	560	1250	0.08	5.22
0.060	0.058	3682	3619	62.6	20	22	17	310	450	1060	0.12	4.72
0.080	0.070	3614	3545	68.6	22	28	36	270	385	920	0.16	4.10
0.100	0.082	3501	3391	110.4	25	34	56	240	335	780	0.23	3.52
0.200	0.118	3059	2917	142.6	35	53	154	175	225	350	0.47	1.80
0.300	0.150	2513	2353	160.1	45	66	220	149	180	125	0.72	0.97
0.400	0.175	1984	1822	162.5	52	80	266	130	152	60	1.00	0.66
0.500	0.190	1497	1371	125.9	60	94	303	122	135	32	1.24	0.48
0.600	0.198	1087	974	112.7	75	120	332	110	115	25	1.50	0.36
0.700	0.212	734	646	88.2	142	195	356	85	87	20	1.76	0.26
0.800	0.240	456	397	59.7	287	350	374	57	60	18	2.02	0.17
0.900	0.325	240	196	43.1	615	710	386	35	35	15	2.52	0.10
0.920	0.375	175	135	40.4	750	850	388	30	30	10	2.72	0.08
0.960	0.600	107	61.8	45.8	1120	1250	391	18	18	5	3.50	0.05
0.980	0.760	77.3	39.9	37.4	1650	1740	393	12	12	—	—	—
1.000	1.000	32.8	—	32.8	—	—	—	—	—	—	—	—

* In this table, all commas represent decimal points.

TABLE 1 (continued)

[illegible]

SODIUM-BUTADIENE RUBBER-BENZENE-BUTYL ALCOHOL

[illegible]

The average values of the partial molar entropy of the components were calculated from the equations:

$$\Delta \bar{S}_1 = \frac{\Delta \bar{H}_1 - \Delta \bar{F}_1}{T} \quad (3)$$

$$\Delta \bar{S}_2 = \frac{\Delta \bar{H}_2 - \Delta \bar{F}_2}{T} \quad (3a)$$

The values thus obtained for the thermodynamic functions of low-molecular components in the high-polymer phase of natural rubber-methyl alcohol-



Fig. 4.—Initial sections of curves of the degree of swelling (Q) vs. composition of the equilibrium solution (N_2): Curve 1. Natural rubber-benzene-methyl alcohol. Curve 2. Natural rubber-benzene-ethyl alcohol. Curve 3. Natural rubber-benzene-butyl alcohol.

The ordinate indicates $Q \frac{\text{mg.}}{\text{g. rubber}}$

benzene, natural rubber butyl alcohol-benzene, and synthetic rubber-butyl alcohol-benzene systems are shown in Table 1.

INTERPRETATION OF THE EXPERIMENTAL DATA

The selective nature of the absorption of the components of the system, which is characterized by the deviation of the curve of the molar fraction of alcohol in the polymer phase as a function of the molar fraction of the equilibrium solution from the line joining the points $N_2^a = 0$ and $N_2^a = 1$, is most pronounced in systems with methyl alcohol and is less for systems with butyl alcohol. Thus, for the same polymer, the selectivity of absorption decreases in the same direction as the intensity of the energy of cohesion of the alcohols. If the capacities of both polymers studied here for selective absorption are compared, it is seen that, for a given alcohol, the selectivity of absorption is much more pronounced for the vulcanizate of butadiene rubber than for vulcanized natural rubber.

TABLE 2*
VALUES OF THE DISTRIBUTION COEFFICIENTS OF ALCOHOL AND BENZENE BETWEEN A HIGH POLYMER
AND A BINARY SOLUTION

	Natural rubber						Butadiene rubber						Q
	K ₀	K ₁	-ΔF	ΔH	ΔH ^a	ΔS	K ₀	K ₁	-ΔF	ΔH	ΔH ^a	ΔS	
Alcohol	1	2	3	4	5	6	7	8	9	10	11	12	13
Methyl alcohol	1.25	12.50	130	-1600	1900	-5.0	1.15	20.00	81	-1550	1950	-5.0	3500
Ethyl alcohol	1.15	10.50	81	-1500	2200	-4.8	1.00	14.30	0	-1520	2180	-5.2	3700
Butyl alcohol	1.00	7.30	0	-400	3500	-1.4	0.90	8.70	-58	-900	3000	-3.3	3900

* In this table, all commas represent decimal points.

The initial sections of the degree of swelling-composition curves in systems with natural rubber are shown in Figure 4.

Comparison of the curves in Figure 4 and columns 1 and 2 of Table 1 shows that the maximums on the curves of isothermic equilibrium conform to Kononov's law. On the curve of isothermic equilibrium in the natural rubber-benzene-methyl alcohol system, the maximum is most pronounced, and appears at $N_2 = 0.05$. With increase of the molecular weight of the alcohol, the height of the maximum falls, and the state at which it appears is displaced toward more dilute alcohol solutions. In butadiene rubber, the maximums are shifted toward benzene.

The coefficients of distribution of alcohol, K_2 , and benzene K_1 , between the high-molecular and binary solutions were determined for both polymers from the initial slopes of the $N_2^n - N_2$ curves at $N_2 = 0$ and $N_2 = 1$, respectively. The values of these coefficients are shown in Table 2.

It follows from the data in Table 2 that, in each of the systems studied, natural rubber is characterized by a larger coefficient of distribution of alcohol and, correspondingly, a smaller coefficient of distribution of benzene than is butadiene rubber. Hence, the decrease of free energy in the transfer of 1 mole of alcohol from an infinitely dilute benzene solution to the polymer phase is larger for natural rubber than for butadiene rubber. On the other hand, the decrease of free energy during the transfer of 1 mole of benzene from an infinitely dilute alcohol solution is greater for butadiene rubber. These effects are evidently the result of the smaller double-bond content of the main chains of the molecules of sodium-butadiene rubber and its lesser tendency to oxidize.

It is important to explain what type of bond is formed by the alcohol molecules with the polar groups of polymers. The change of free energy which accompanies the passage of 1 gram-mole of alcohol from an infinitely dilute alcohol solution into the polymer and the coefficient of distribution of alcohol between the polymer and solution are related by the equation:

$$\Delta F = -RT \cdot \ln K \quad (4)$$

The change of heat content in the passage from pure alcohol to the polymer will be designated by ΔH^* , the change of heat content in the passage from pure alcohol to an infinitely dilute solution in benzene by Q , and the change of heat content for the passage of 1 gram-mole of alcohol from an infinitely dilute solution to the polymer by ΔH . On the basis of Hess' law:

$$\Delta H = \Delta H^* - Q \quad (5)$$

The values of ΔH^* were obtained by extrapolating the experimental data for partial heats of dilution of alcohols in the polymer phase to $N_2 = 0$ (see column 11 of Tables 1 and 2). The heats of solution of alcohols in benzene at infinite dilution are taken from Wolf. The values of ΔH , calculated according to Equation (5), are shown in Table 2 for both polymers studied. In the same table are recorded the changes of entropy for the passage from infinitely dilute solution to the polymer, calculated according to the equation:

$$\Delta S = \frac{\Delta H - \Delta F}{T} \quad (6)$$

It is seen from column 4 of Table 2 that the transfer of 1 gram-mole of methyl alcohol from an infinitely dilute solution into natural rubber is accompanied by the liberation of 1600 calories. Approximately the same amount of heat is

liberated in the passage of 1 gram-mole of methanol into butadiene rubber. Since this is much less than the energy of the hydrogen bond, the assumption that alcohol molecules react with the polar groups of polymers "according to the type" of hydrogen bond is incorrect. The calculations shown in Table 2 confirm the dipole-dipole character of this reaction, as described earlier by one of the authors⁴. This theory is also confirmed by the fact that the ΔH values are not constant in a homologous series of alcohols, but decrease with an increase of the molecular weight of the alcohols. This can be explained by the fact that the steric hindrance to dipole-dipolar reactions increases in proportion to the length of the hydrocarbon chain.

The passage from infinitely dilute solution into a polymer is accompanied by a comparatively small decrease of entropy. For example, for methyl alcohol, the decrease of entropy is 5 cal./degree-gram-mol., while the passage

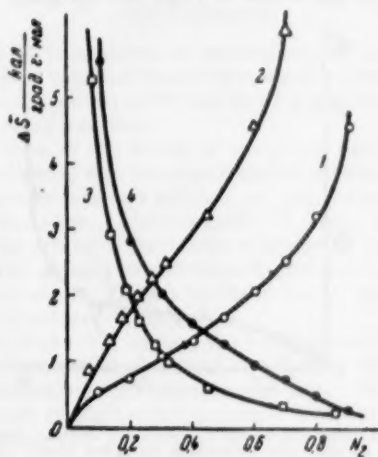


Fig. 5.—Curves of the partial molar entropy vs. composition of a natural rubber-benzene-butyl alcohol system. Curve 1. Partial entropy of benzene in the solution. Curve 2. Partial entropy of benzene in the polymer. Curve 3. Partial entropy of alcohol in the polymer. Curve 4. Partial entropy of alcohol in the solution. The ordinate indicates $\Delta \bar{S} \frac{\text{cal.}}{\text{degree. g.-mol.}}$.

from vapor to liquid is accompanied by a decrease of entropy equal to 40.6 cal./degree-gram-mol. From the data on the change of entropy, it must be concluded that alcohol molecules are fixed about the polar groups of the polymer (principally the double bonds) weakly, and the mobility of the alcohol molecules in the polymer phase increases with increase of molecular weight. Otherwise it is difficult to explain the increase of entropy in the passage from methyl alcohol to butyl alcohol.

We shall compare the thermodynamic functions of the low-molecular components in binary solution and in the polymer. The values of partial molar entropy of benzene and alcohol of both phases as a function of the composition for a natural rubber-benzene-butyl alcohol are shown in Figure 5.

It is seen from Figure 5 that the partial entropy of benzene is larger in the polymer phase for the same composition. In the passage of benzene to the polymer phase, there is an additional increase (compared with a binary solu-

tion) of the number of configurations between the benzene molecules and segments of the polymer chains. It is further seen that the passage of alcohol into the polymer phase is accompanied by a smaller increase of entropy than in the passage of the same compound into binary solution. This means that, in the polymer phase, the alcohol molecules are in a more ordered state, because they are fixed principally about the polar groups. This leads to a decrease of the number of possible configurations between the alcohol molecules and benzene molecules in the polymer phase.

Since the partial heat content values for low-molecular components in the polymer phase are positive (heat is absorbed), the decrease of free energy during the sorption of low-molecular components by the polymer from the binary systems studied here is due exclusively to the increase of entropy of the two components. For the sorption of single liquids by a high polymer, this phenomenon is evident in the studies of Tager and Kargin¹⁰.

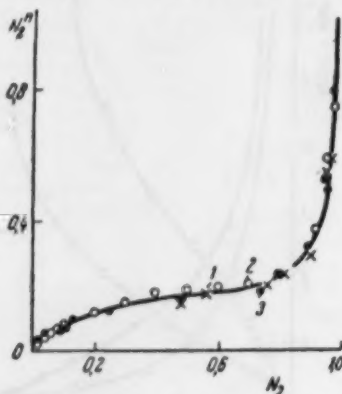


Fig. 6.—Distribution in the benzene-methyl alcohol-polymer system. Point 1. Purified natural rubber. Point 2. Vulcanized natural rubber (containing no carbon black). Point 3. Protected rubber, loaded with carbon black and whiting.

Comparison of the data of Table 1 shows that a larger increase of entropy of alcohol is observed in butadiene rubber than in natural rubber. These facts are evidently explainable by the lower content of free oxidized groups in butadiene rubber. The larger the polar group content of the polymer, the greater is the probability of uniform distribution of the alcohol molecules among the chains of the polymer; and, on the other hand, a decrease of the number of polar groups must cause a more ordered distribution of the alcohol molecules among the polymer chains.

Because of the reaction with the polar groups of the alcohol molecules, an increase of the number of polar groups in the polymer leads to an increase of the potential rotation barriers, a decrease of elasticity of the chains, and, consequently, a decrease of the entropy of benzene. With elongation of the hydrocarbon chain, the reaction of the polar groups of the alcohol and polymer becomes weaker, and the differences in the thermodynamic behavior of natural and butadiene rubber almost disappear. This may be seen by a comparison of the data of Table 2.

The question naturally arises whether the shape of the curve of equilibrium between the polymer and binary solution depends on the composition of the

rubber. The data obtained here in the study of the distribution between vulcanized natural rubber and a benzene-methyl alcohol system will be compared with the data obtained by one of the authors in a study of the behavior in the same system of vulcanized natural rubber containing 35 parts by weight of lampblack and 50 parts by weight of whiting per 100 parts of rubber⁴, as well as a purified natural rubber prepared by precipitation from benzene solution by alcohol. The results of the study of distribution obtained for pure rubber and two different vulcanizates are shown in Figure 6, where it is evident that the distribution between the polymer and binary solution is determined by the nature of the polymer, and is practically independent of its composition.

The experimental data of the present study are further confirmation of the conclusion of Gul concerning the necessity of considering the non-uniformity of the force field of intermolecular reaction in rubber¹¹.

CONCLUSIONS

1. The swelling of vulcanizates of natural rubber and sodium-butadiene rubber in the saturated vapors of binary systems of benzene and low-molecular alcohols (from methyl to butyl) at 20° and 50° C was studied in the entire range of composition of binary solutions.

2. The general form of the curves of isothermic equilibrium between the swollen polymer and binary solution were found to conform to Konovalov's law.

3. The absorption of a binary solution by both polymers has a very pronounced selective character. The selectivity of absorption of the solution is more pronounced, the greater is the density of energy of cohesion of the alcohol. In natural rubber, the capacity of selective absorption is more pronounced than in sodium-butadiene rubber. This is probably due to the larger concentration of oxidized groups in natural rubber.

4. The changes of the free energy, the heat content, and entropy for the passage of one gram-mole of alcohol from an infinitely dilute solution into the polymer were calculated from the experimental data. These calculations indicate that the reaction of the alcohol molecules with the polar groups of the polymer is dipole-dipole.

5. The passage from pure benzene to a swollen polymer of any particular composition is characterized by a large increase of entropy in comparison with the passage to a binary solution of the same composition. The relation in alcohol is the reverse. The increase of the entropy of benzene can serve as a measure of the elasticity of the polymer chains. A decrease of the entropy of alcohols indicates the content of free polar groups in the polymer phase.

6. The values of the partial heat content of the low-molecular components are positive; consequently, the decrease of free energy during their sorption by the polymer is due exclusively to an increase of entropy.

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VULCANIZATION OF CREPE RUBBER BY SULFUR MONOCHLORIDE. II. THE DILATOMETRIC METHOD *

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INTRODUCTION

The vulcanization of rubber by sulfur monochloride is believed to consist of the cross-linking of adjacent isoprene units by thio-ether bonds¹. Such a reaction, involving polymer aggregation, should be accompanied by an increase of the density of the rubber, and, by choosing a suitably delicate technique, it should be possible to measure the rate of vulcanization by observing density changes. A dilatometric method seemed most suitable, and it was found that the reaction could indeed be followed by observing the rate of decrease of volume of the system rubber-sulfur monochloride when dissolved in a suitable solvent².

Initial experiments showed that, during cold vulcanization, the system underwent a volume contraction which was of the order of 10 per cent with respect to the rubber. This comparatively large contraction allowed one to work with extremely dilute solutions ($<0.3\%$ w/w) of rubber. It thereby became possible to study the systems under more ideal kinetic conditions of high dilution than has been hitherto possible. In the present investigation, it has not been possible to do more than establish the broad outlines of the kinetic behavior of the system, and, on this basis, to propose feasible mechanisms for the cold vulcanization process.

EXPERIMENTAL

The dilatometer has already been described elsewhere³, and is shown in Figure 1. The instrument contains a tap which allows high sensitivity combined with quick filling. The dilatometer was filled by dipping the coarse capillary in the reaction mixture and applying suction (water pump) through the fine capillary. Preliminary experiments showed that no leakage was detectable when an aqueous sugar grease was used as a tap lubricant. All kinetic runs were performed in a precision thermostat (sensitivity $\pm 0.0003^\circ \text{C}$) at 25.0°C , which was heated by a permanent low-power heater, together with a variable low-power intermittent heater connected through a Sun-Vic relay to a toluene regulator. The meniscus height was read through a telescope to avoid parallax errors.

Crepe rubber, supplied as a 20 per cent gel in benzene, was purified by dispersing in redistilled thiophene-free benzene and precipitating with redistilled dry ethanol. The process was repeated twice, and the final product was freed from solvent by Hyvac treatment.

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The solvents used in the kinetic studies were purified by standard methods, dried by standing over anhydrous sodium sulfate, and distilled.

Sulfur monochloride was purified by distilling twice from sulfur and charcoal. The final product was a golden yellow liquid, b.p. 137° C.

A commercial accelerator (Butyl-8) was used as supplied, and is believed to consist of dibutylammonium thiocarbamate 34 per cent, 2-mercaptobenzothiazole 21 per cent, and Cellosolve 45 per cent. A pure sample of 2-mercaptobenzothiazole (MBT, m.p. = 180°)⁴ and dibutylammonium dibutyldithiocarbamate (DBA)⁵ were used in the experiments.

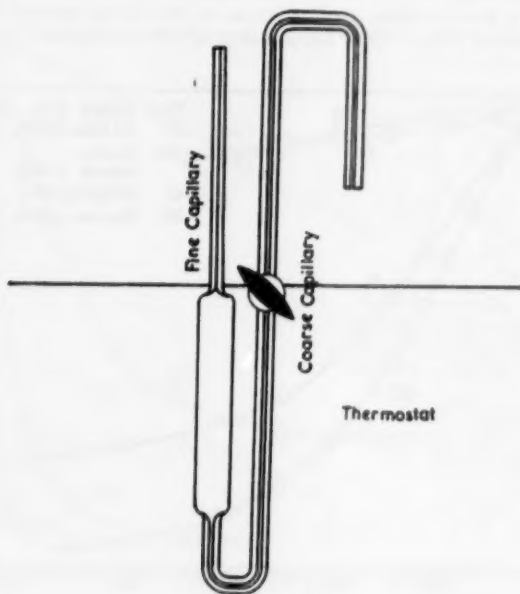


FIG. 1.—Tap dilatometer.

RESULTS AND DISCUSSION

NONACCELERATED REACTIONS

Effect of Solvent

The first part of the dilatometric investigation was concerned with the effect of the solvent on the extent and rate of the vulcanization process. A series of rubber dispersions (about 0.2 per cent) in petroleum ether (b.p. 100–120°), cyclohexane, benzene, and a 25–75 per cent (v/v) mixed solvent of chloroform and carbon tetrachloride was prepared. Vulcanization rates were measured in the presence of excess sulfur monochloride at 25° C. Results are shown in Figure 2, where it can be seen that, in the extremely nonpolar solvents, petroleum ether and cyclohexane, the volume contraction is slight. On the other hand, in the more polar solvents, benzene and chloroform-carbon tetrachloride, the volume contraction is appreciably greater. It was significant that

the unvulcanized rubber dispersions in both petroleum ether and cyclohexane exhibited a marked Tyndall effect. In the solvents, benzene and chloroform-carbon tetrachloride, however, the unvulcanized dispersions were transparent. It is evident, therefore, that, in the bad solvents, petroleum ether and cyclohexane, we have comparatively large aggregates of rubber, whereas, in the good solvents benzene and chloroform-carbon tetrachloride, we are approaching molecular dispersion.

Since, in all cases, the final products of vulcanization are eventually precipitated from solution, it is clear that the extent of chemical reaction should depend very strongly on the state of aggregation of the rubber in the various solvents. In a good solvent, such as benzene, the sulfur monochloride molecules are presented with a highly accessible array of unsaturated isoprene units;

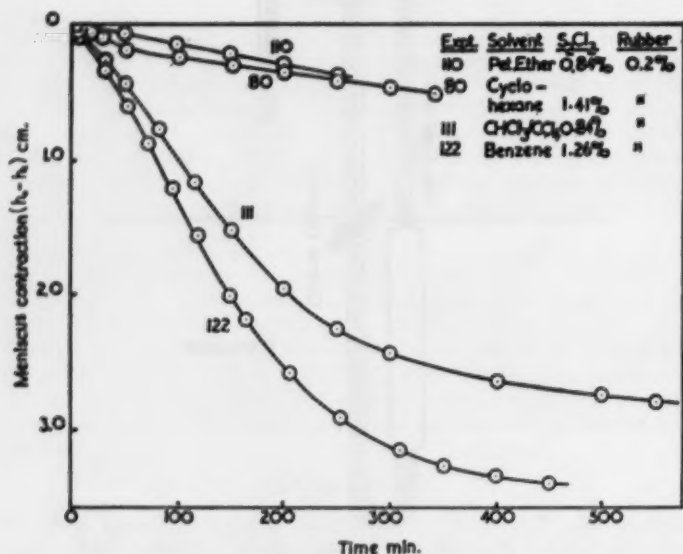
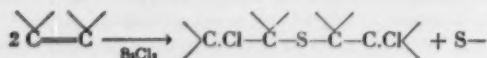


Fig. 2.—Effect of solvent on vulcanization kinetics at 25° C.

in a bad solvent, such as petroleum ether, the sulfur monochloride is presented with the surface of an aggregate of rubber molecules. The final, vulcanized product should, therefore, vary in its chemical constitution from solvent to solvent. It is to be expected that, in petroleum ether, the final precipitate of vulcanized rubber will consist of clusters of unvulcanized rubber, held together by a surface network of vulcanized rubber. In a good solvent, on the other hand, we may expect to approach more completely the idealized reaction proposed by Meyer and Mark¹, i.e.:



Having established the importance of the solvent on the state of aggregation of the rubber and, hence, on the extent of vulcanization, the next stage was to

study the effect of the solvent on the rate of vulcanization. For this purpose, we prepared dispersions of rubber (about 0.2 per cent) in a series of mixed solvents ranging from 100 per cent chloroform to 100 per cent carbon tetrachloride. Dilatometric runs were then performed on these dispersions in the presence of an excess (0.84 per cent w/v) of sulfur monochloride at 25° C. Results are shown in Figure 3, where it can be seen that both the rate and the extent of reaction are strongly dependent on the chloroform content of the mixed solvent. Although the reaction was not kinetically of pure first-order type, it was possible to calculate first order rate coefficients (k_1) over an appreciable range of the reaction. These are plotted in Figure 3 (inset) as a function of the

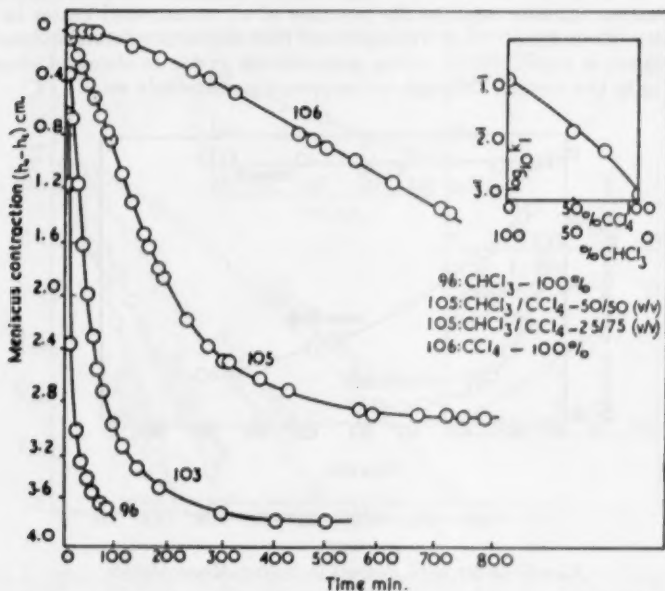


Fig. 3.—Effect of solvent on rate of vulcanization in mixed chloroform-carbon tetrachloride solvents at 25° C. Inset: Plot of $\log k_1$ against solvent composition.

nature of the solvent and it is seen that the reaction is about 100 times faster in chloroform than in carbon tetrachloride. The reaction is thus facilitated by the more polar solvent, chloroform. It is not yet clear whether this implies a polar mechanism for the reaction, or whether the reaction is being catalyzed by the chloroform, i.e., by H atoms or CCl_3 radicals.

Reaction with Model Compounds

In the course of the present investigation, it was noticed that the reaction, as characterized by the volume contraction of the system, was accompanied by the development of a strong Tyndall effect. This being so, it was feasible that the incipient precipitation of the vulcanized rubber might be the cause of the volume contraction, i.e., the rate of the vulcanization, determined dilatometrically, might be "rate of Tyndall formation" and not the rate of chemical reaction

(unless these are identical). In order to clarify this point, it was decided to "vulcanize" a compound which would remain dissolved in the solvent throughout the reaction. A suitable compound was glyceryl trioleate, which contains the requisite ethylenic linkages for the cross-linking reaction. Figure 4 shows two dilatometric reaction curves for glyceryl trioleate and sulfur monochloride in benzene. Careful observation showed that the reaction mixture remained wholly transparent throughout the period of reaction. It can be seen that a marked contraction takes place, and that the rate is increased by the addition of the accelerator Butyl-8 (0.050 per cent). A parallel experiment (see Figure 4), using glyceryl trilaurate—which contains no ethylenic linkages—showed no detectable reaction. This confirms the hypothesis that the cold vulcanization reaction requires the presence of an unsaturated center in the molecule. From the above, it was concluded that the volume decrease observed when rubber is vulcanized by sulfur monochloride is due to chemical changes occurring in the system, although not necessarily exclusively so.

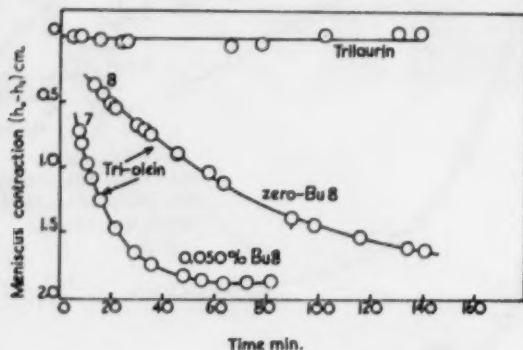


Fig. 4.—Reaction curves for trilaurin and triolein with sulfur monochloride at 25° C. Solvent: benzene.

Kinetic Order with Respect to Sulfur Monochloride

Figures 2 and 3 show that the nonaccelerated reaction-time curves are autocatalytic in nature, i.e., the reaction commences slowly, attains a maximum rate, and subsequently slows down until reaction is complete. Since the slower initial portion of the reaction curve tends to linearity, it becomes possible to characterize the initial rate of reaction by the slope of the curve in this region. We thereby obtain an empirical zero-order rate coefficient (k_0) which may be expressed in millimeters of contraction per minute. By considering the later stage of the reaction, one may characterize the reaction rate by the slope of the logarithmic plot, and obtain a first order rate coefficient (k_1). We are thus enabled to describe the whole of the reaction in terms of k_0 for the initial rate and k_1 for the subsequent rate.

In order to simplify the kinetic form of the reaction, runs were performed in the presence of a stoichiometric excess of sulfur monochloride. Thus, Figure 5 summarizes the salient kinetic features of a block of runs carried out on about 0.2 per cent rubber/benzene dispersion in the presence of varying amounts of sulfur monochloride, the latter being in excess (1.2 to 4.0 per cent)

throughout. Figure 5(a) shows a series of logarithmic plots for such a block of runs, and it may be calculated that the reaction does not become first order until 40 per cent of the total reaction has proceeded. In Figures 5(c) and (d), the rate coefficients k_2 and k_1 are plotted as a function of the sulfur monochloride concentration. Both relationships are linear and show that the whole of the reaction is kinetically of the first order with respect to sulfur monochloride. This result is important mechanistically, since it demonstrates that the rate-determining stage(s) involves either the undissociated sulfur monochloride molecule or an asymmetric fission product (viz., $\dot{S}-S-Cl$ or $\overset{+}{S}-S-Cl$). It cannot involve, for example, a symmetric fission product such as $\dot{S}-Cl$. A

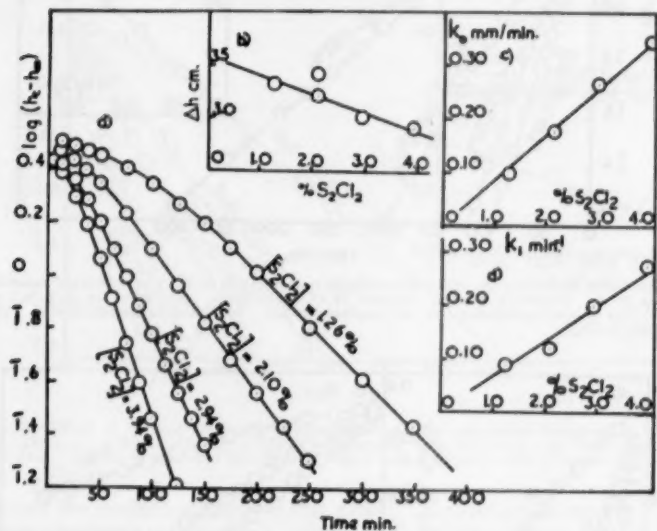


Fig. 5.—Effect of varying the sulfur monochloride concentration on the nonaccelerated vulcanization reaction at 25° C. [Rubber] = 0.2%. Solvent: benzene. (a) Plot of $\log(h_t - h_\infty)$ against time. (b) Plot of total contraction (Δh , cm.) against $[S_2Cl_2]$. (c) Plot of k_2 against $[S_2Cl_2]$. (d) Plot of k_1 against $[S_2Cl_2]$.

parallel set of experiments carried out in a mixed chloroform-carbon tetrachloride (25/75) solvent (Figure 6) showed the same general features as were found in benzene.

A point worthy of note is that the total extent of vulcanization depends markedly on the amount of vulcanizing agent present. This is illustrated in Figures 5(b) and 6(b), which show plots of the total contraction (Δh , cm. of meniscus height) against sulfur monochloride concentration. In the mixed chloroform-carbon tetrachloride solvent, it is seen that the presence of 4 per cent sulfur monochloride is sufficient to reduce the total contraction by about 35 per cent.

ACCELERATED REACTION

Nature of Kinetics of Accelerated Reaction

It has been shown that the nonaccelerated reaction is kinetically of the first order with respect to sulfur monochloride. The first step in studying the ac-

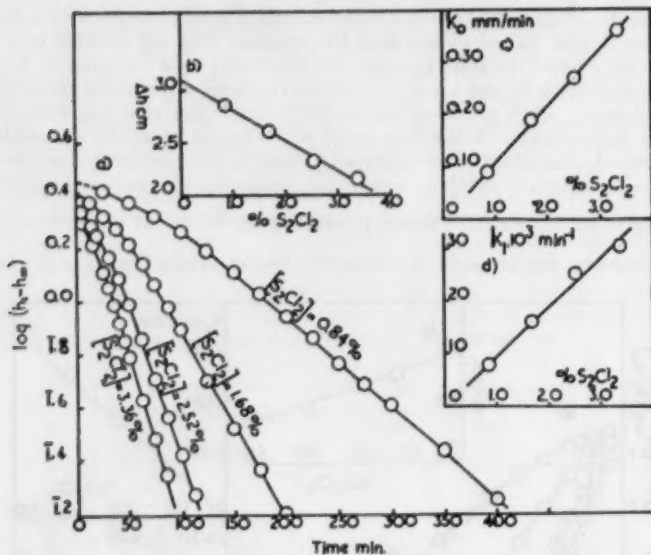


FIG. 6.—Effect of varying the sulfur monochloride concentration on the nonaccelerated vulcanization reaction at 25° C. [Rubber] = 0.2%. Solvent: 75 CCl_4 /25 $CHCl_3$. (a) Plot of $\log(h_t - h_\infty)$ against time. (b) Plot of total contraction (Δh , cm.) against $[S_2Cl_2]$. (c) Plot of k_0 against $[S_2Cl_2]$. (d) Plot of k_1 against $[S_2Cl_2]$.

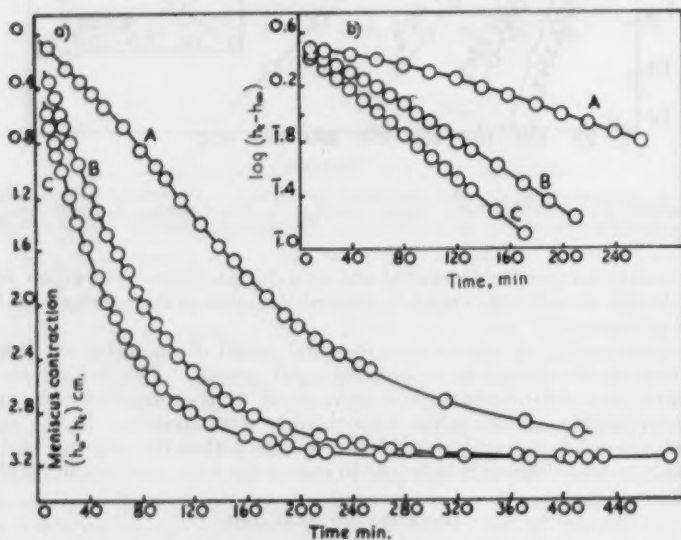


FIG. 7.—(a) Effect of Butyl-S accelerator on the rate of vulcanization at 25° C. [Rubber] = 0.2%. $[S_2Cl_2]$ = 1.4%. Solvent: benzene. A = zero Bu S, B = 0.020% Bu S, C = 0.035% Bu S. (b) Plot of $\log(h_t - h_\infty)$ against time.

celerated reaction was to ascertain the nature of the reaction curve in the presence of an accelerator. The accelerator chosen to initiate the study was Butyl-8. This accelerator is known to increase the rate of vulcanization as measured by the gelation technique⁶. Two blocks of runs were accordingly performed, in which the initial concentration of sulfur monochloride was con-

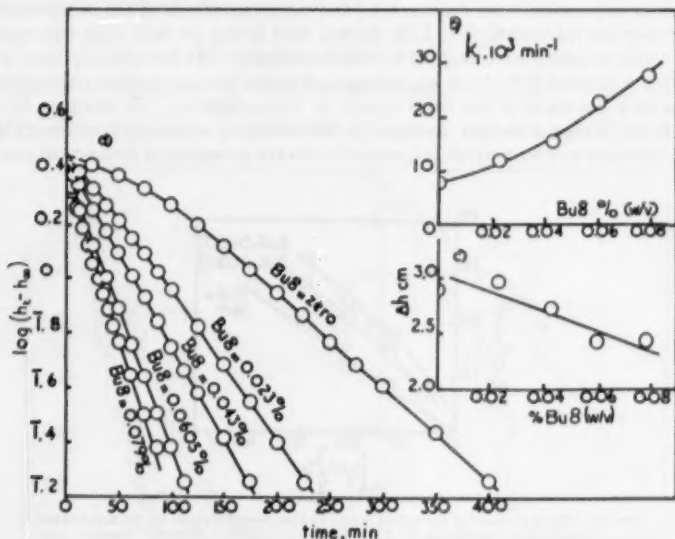


Fig. 8.—Effect of varying the Butyl-8 concentration on the accelerated vulcanization reaction at 25° C. [Rubber] = 0.2%. $[S_2Cl_2]$ = 0.84%. Solvent: 75 CCl_4 /25 $CHCl_3$. (a) Plot of $\log(h_t - h_\infty)$ against time. (b) Plot of k_1 against [Bu-8]. (c) Plot of total contraction (Δh , cm.) against [Bu-8].

stant and the amount of Butyl-8 was varied. Results are plotted in Figure 7 (solvent: benzene) and Figure 8 (solvent: chloroform-carbon tetrachloride).

With benzene as solvent, the experimental details are given in Table I. Figure 7(a) shows the nonaccelerated reaction (curve A) with its slow initial portion developing, after about 120 minutes, into a first-order reaction. In the presence of small amounts of accelerator (curves B and C), two effects are ap-

TABLE I

Expt.	$[S_2Cl_2]$, %	[Bu-8], %	k_1 , min. ⁻¹
A	1.4	0	0.0078
B	1.4	0.020	0.0152
C	1.4	0.035	0.0189

parent: the slow initial reaction is eliminated as a rate-determining factor, and the rate coefficient (k_1) of the subsequent first-order reaction is markedly increased. Figure 7(b) is logarithmic and shows both the catalytic effect of the accelerator and how the first-order portion of the reaction has been extended from 55 per cent of total reaction in A to 80 per cent in C. The latter value covers the whole of the experimentally observed region.

With the mixed chloroform-carbon tetrachloride solvent, and with a somewhat smaller concentration of sulfur monochloride, the same general features were observed. Results are illustrated in Figure 8(a), which clearly shows that, as the amount of Butyl-8 is increased up to 0.04 per cent, the slow, initial portion of the reaction is gradually eliminated. Above 0.04 per cent Butyl-8, the reaction becomes one of pure first order over the whole of the experimentally observed region. In Figure 8(b) the catalytic effect of the accelerator on the first-order rate coefficient k_1 is shown, and it can be seen that the reaction order tends to unity with respect to the accelerator. It has already been noted (Figures 4(b) and 6(b) that an increase of sulfur monochloride concentration results in a decrease of the total extent of vulcanization. It can now be seen (Figure 8(c)) that a similar decrease of the extent of vulcanization occurs when the accelerator concentration is increased—in the presence of a constant amount

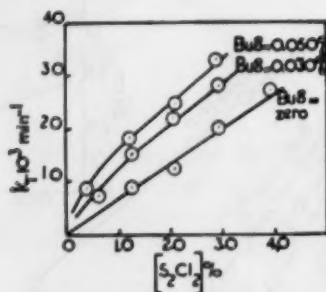


Fig. 9.—Effect of varying the sulfur monochloride concentration on the accelerated vulcanization reaction at 25° C. [Rubber] = 0.2%. Solvent: benzene.

of sulfur monochloride. This suggests that the extent of vulcanization depends on the velocity of the process, irrespective of the reagent effecting the increase of velocity.

Kinetic Order with Respect to Sulfur Monochloride

Having established that the nonaccelerated reaction is kinetically of the first order with respect to the sulfur monochloride, it became of interest to determine the kinetic order of the reaction with respect to the same reagent in the presence of the accelerator, Butyl-8. Two blocks of runs were, therefore, performed in benzene, in which the sulfur monochloride concentration was varied in the presence of fixed amounts of Butyl-8. First-order rate coefficients (k_1) are plotted in Figure 9 against sulfur monochloride concentration. Also shown is the appropriate plot of the corresponding nonaccelerated reaction. Whereas the relationship for the nonaccelerated reaction is completely linear, the accelerated relationship is not quite linear—there being a definite deviation below 1 per cent sulfur monochloride. The reason for this deviation is not clear; it seems to be connected with the disappearance of the slow, initial stage in the accelerated reaction. However, apart from this initial deviation, the accelerated reaction is clearly first order with respect to the sulfur monochloride.

Effect of Mercaptobenzothiazole

One of the active components of Butyl-8 is 2-mercaptobenzothiazole (MBT). This compound exerted a marked accelerating effect on the gelation process⁶. In Figure 10, two dilatometric runs are shown which illustrate the accelerating effect of MBT on the vulcanization process. It remains to investigate this effect in a quantitative manner so as to obtain the kinetic order of the reaction towards MBT.

Effect of Dibutylammonium Dibutyldithiocarbamate

Another component of Butyl-8 is dibutylammonium thiocarbamate, $^{\oplus}\text{N}(\text{Bu})_2\text{H}_2\text{S}^{\ominus}\text{CS}-\text{NH}_2$. Since this compound was not available, kinetic

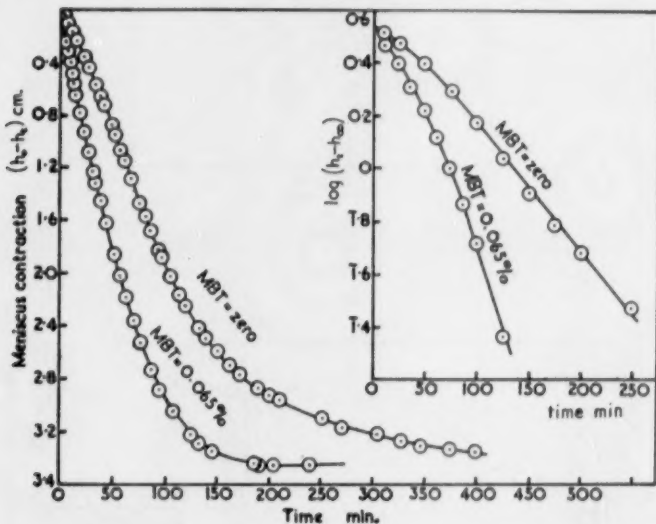


Fig. 10.—Effect of 2-mercaptobenzothiazole (MBT) on the vulcanization reaction at 25° C. [Rubber] = 0.3%. $[\text{S}_2\text{Cl}_2]$ = 2.10%. Solvent: benzene. Inset: Plot of $\log (h_t - h_0)$ against time.

runs were performed on the analogous dibutylammonium dibutyldithiocarbamate (DBA), $^{\oplus}\text{N}(\text{Bu})_2\text{H}_2\text{S}^{\ominus}\text{CS}-\text{N}(\text{Bu})_2$. These are shown in Figure 11. It can be seen from Figure 11(b) that the accelerating effect seems to depend linearly on the DBA concentration. This suggests the catalyzing entity to be the single molecule (or a derivative, such as $\text{H}-\text{S}-\text{CS}-\text{N}(\text{Bu})_2$). A point worthy of note from Figure 11(a) is that DBA eliminates the slow, initial portion of the reaction (cf. MBT which does not appear to do this, Figure 10 inset).

Effect of Methanol

Gelation experiments⁶ led us to attempt to use amines and diamines as accelerators. However, it soon became clear that they were unsuitable for dilatometric investigation, since they reacted immediately with the sulfur

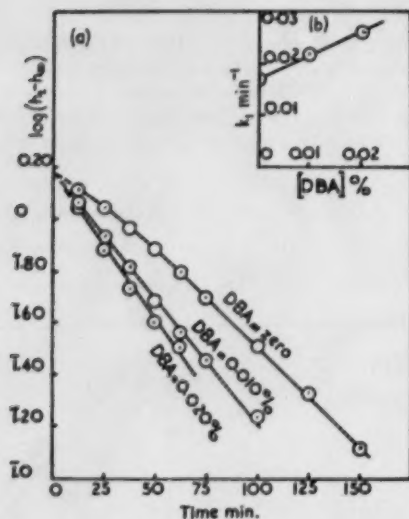


FIG. 11.—Effect of DBA on the vulcanization reaction at 25° C. [Rubber] = 0.1%. $[S_2Cl_2]$ = 2.10%. Solvent: benzene. (a) Plot of $\log (h_t - h_\infty)$ against time. (b) Plot of k_1 against [DBA].

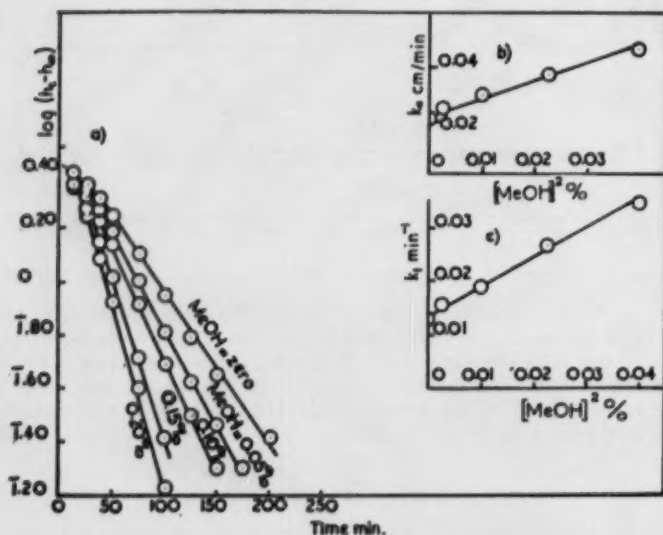


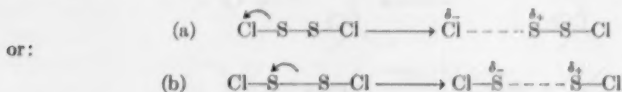
FIG. 12.—Effect of methanol on the vulcanization reaction at 25° C. [Rubber] = 0.3%. $[S_2Cl_2]$ = 2.10%. Solvent: benzene. (a) Plot of $\log (h_t - h_\infty)$ against time. (b) Plot of k_2 against $[MeOH]^2$. (c) Plot of k_1 against $[MeOH]^2$.

monochloride to produce a thick flocculant. This posed the question of side reactions and side precipitations taking place in the dilatometer contemporaneously with the vulcanization. Clearly the system was unfavorable.

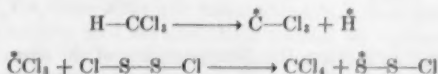
Finally, methanol was chosen as a suitable compound. This remained in solution through the whole of the reaction. Results are shown in Figure 12(a), where the accelerating effect is well illustrated. In Figures 12(b) and 12(c), the rate coefficients k_0 and k_1 are plotted as a function of the square of the alcohol concentration. The relationship is linear, thus suggesting that two molecules of alcohol are involved in the rate-determining stage of the accelerated reaction. This result confirms the analogous conclusion derived previously from gelation data⁶.

MECHANISTIC CONSIDERATIONS

The first point to be discussed is whether the reaction involves homolytic (free radical) or heterolytic (polar) bond fission. Our results, up to the present, do not provide a definite answer. For example, in Figure 2 (inset) it is shown that chloroform is a faster solvent (about 100 times) than carbon tetrachloride for the nonaccelerated reaction. This suggests a polar mechanism for the nonaccelerated reaction, possibly involving the heterolytic fission of the sulfur monochloride molecule, thus:



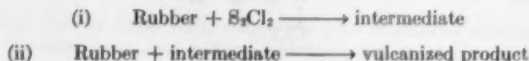
On the other hand, the facile nature of the reaction in such a nonpolar solvent as benzene is evidence against such a polar mechanism. It may very well be that the reaction is indeed nonpolar and that it is being chemically accelerated by chloroform via the radical CCl_3 , which is activating the homolytic fission of the $\text{Cl}-\text{S}$ bond of sulfur monochloride:



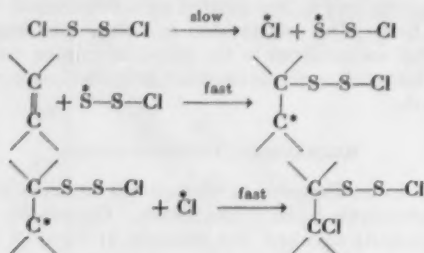
The radical mechanism for the reaction is supported by the chemical nature of the accelerators⁶. These were found to be most effective when possessing an active hydrogen atom such as occurs in the groups $-\text{NH}-$, $-\text{SH}$, $-\text{OH}$. Since the gelling rate showed no correlation with the acidity of the accelerators of type $\text{R}-\text{H}$, it must be concluded that the accelerator functions by means of a free radical mechanism, such as, for example:



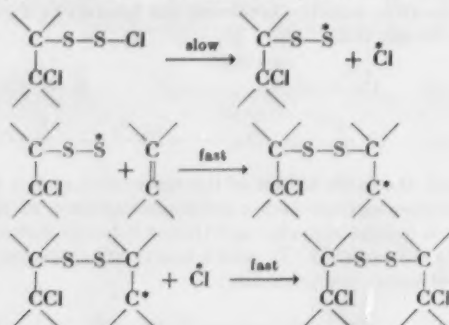
The autocatalytic nature of the nonaccelerated vulcanization reaction suggests that we are observing (at least) two consecutive processes taking place with comparable rate coefficients, and that one of the products of the initial reaction (i) becomes a reactant in the later reaction (ii), thus:



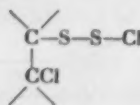
The initial, slow part of the reaction curve thus corresponds to an increase in the concentration of the intermediate compound and, hence, to an increase in the velocity of reaction (ii)—which is essentially the cross-linking process. A possible sequence of component processes is shown below. Reaction (i) may be interpreted as containing the following stages:



While reaction (ii) would consist of the subsequent series:

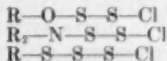


In the accelerated reaction, the disappearance of the slow, initial stage may be explained by the accelerator speeding up the component processes of reaction (i) to such an extent that reaction (i) is no longer rate-determining. The rate of vulcanization is then completely determined by the second, crosslinking process. It is virtually impossible—at this stage—to decide which of the component processes of reaction (i) is catalyzed by the accelerator. There are too many unknown factors at the moment. However, one may provisionally suggest that the accelerator reacts with sulfur monochloride, as previously suggested to give the free radical $\dot{\text{S}}\text{-S-Cl}$. This will augment the supply of $\dot{\text{S}}\text{-S-Cl}$ radicals obtained by thermal dissociation of sulfur monochloride and, hence, speed up the over-all rate of production of the intermediate to such an extent that it is no longer rate-determining. If we identify the intermediate as:

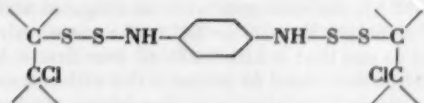


then it is reasonable to suppose that any subsequent reaction of this intermediate will be affected by the usual accelerators, because this intermediate is clearly very similar to sulfur monochloride—thus, they both contain the same functioning group, $-S-S-Cl$. An accelerator may, therefore, be expected to function twice before the cross-linking reaction is complete.

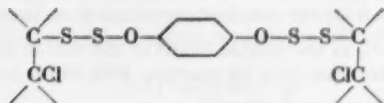
As yet it is not known whether the accelerator is incorporated chemically in the vulcanized molecule and, hence, whether the accelerator is a true catalyst; or whether the accelerator initiates a series of different reactions involving such species as:



in addition to the original sulfur monochloride molecule. The very great effect of bifunctional accelerators such as the phenylenediamines, etc.⁶, suggests that the former concept is nearer the truth, and that the accelerator is actually incorporated in the vulcanizate, possibly by means of the following additional types of cross-linking:



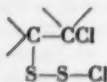
or:



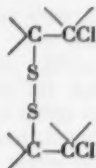
It may be objected that, in the above analysis, we have regarded the final cross-linked polymer as containing the group $C-S-S-C$ rather than the $C-S-C$ group of Meyer and Mark. The reason is that it is by no means convincing that the cross-links are mono thio-ether linkages. The thio-ether theory was originally based on analytical results on vulcanized samples. It seems to the present author that the reaction is by no means as simple as originally thought. For example, present results show that the extent of vulcanization is strongly dependent on several different factors, and there is no evidence to tell us to what extent the product of Meyer and Mark had been vulcanized. Thus, any analytical results must be accepted with great caution. It is clear that a vulcanizate which contains some unreacted units (I) together with some partly reacted units (II), and cross-linked units (III), is likely to



(I)



(II)



(III)

give analytical results that may correspond to exclusive monosulfur bridge formation. Furthermore, it is not yet known to what extent the vulcanization

is accompanied by side reactions, such as rubber hydrochloride formation. Nor yet is it known to what extent the reaction is influenced by the presence of latex serum proteins, which are certainly present to a small extent in the rubber samples. One could predict that such dispersed protein would accelerate the vulcanization reaction, since it contains the necessary accelerating groups, i.e., $-\text{NH}_2$, $-\text{COOH}$, and $-\text{OH}$.

SYNOPSIS

The kinetics of the reaction between natural-rubber hydrocarbon and sulfur monochloride was investigated in dilute hydrocarbon solution by the dilatometric technique. Control experiments with trilaurin and triolein show that the reaction requires unsaturated linkages in the compound to be cold-vulcanized. The extent and rate of the nonaccelerated reaction with rubber is shown to depend strongly on the nature of the solvent. Moreover, the non-accelerated reaction is autocatalytic in nature, and exhibits kinetics that are first order with respect to sulfur monochloride. The accelerating effects, on the reaction, of Butyl-8, mercaptobenzothiazole, dibutylammonium dibutyl-dithiocarbamate (DBA), and methanol were investigated and it is shown that, in the presence of sufficient Butyl-8 or DBA, the autocatalytic nature of the reaction is changed to one that is kinetically of pure first order. The accelerated (Butyl-8) reaction was found to be first order with respect to sulfur monochloride. The accelerated reaction is further shown to be first order with respect to DBA and second order with respect to methanol. A free radical mechanism is proposed for the nonaccelerated reaction, involving attack by the intermediate $\dot{\text{S}}-\text{S}-\text{Cl}$ as the double bonds of the rubber molecule. It is suggested that accelerators function by reacting with sulfur monochloride to produce the active intermediate $\dot{\text{S}}-\text{S}-\text{Cl}$.

ACKNOWLEDGMENT

Thanks are due to J. H. Schulman for much helpful advice.

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- ¹ Meyer and Mark, *Ber.* 61, 1946 (1928).
- ² Glaser, *Nature* 167, 404 (1951).
- ³ Glaser and Turner, *J. Chem. Soc. (London)*, 1949, p. 169.
- ⁴ This sample was kindly supplied by the British Rubber Producers' Research Association.
- ⁵ This sample was kindly supplied by K. C. Roberts of the Anchor Chemical Company.
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THE CURING OF SILICONE RUBBER WITH BENZOYL PEROXIDE *

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INTRODUCTION

Little has been reported about the action of benzoyl peroxide as a vulcanizing agent for silicone rubber. Knowledge of this action seems to be of considerable importance, since benzoyl peroxide is the most widely used vulcanizing agent at the present time.

Apparently no studies of the kinetics of peroxide decomposition in silicones have been undertaken. It is not known quantitatively whether or not the silicones influence the decomposition rate in the way some of the solvents studied by Cass¹ and by Nozaki and Bartlett² do.

In this paper we report the results of work undertaken to determine the number of cross-links introduced into polydimethylsiloxane by benzoyl peroxide during the normal vulcanizing process. The apparent efficiency of cross-link production has been determined as a function of the concentration of peroxide, the method of vulcanization, and of the filler content of the sample.

EXPERIMENTAL

MATERIALS

The silicone gum rubber used in this study was a polydimethylsiloxane, prepared by heating octamethylcyclotetrasiloxane with potassium hydroxide, as recommended by Hyde³. It was found by light scattering to have a weight-average molecular weight of 782,000. The benzoyl peroxide used was a purified grade⁴. The silica filler⁵ was found to give good physical properties when incorporated into the gum in the standard fashion. The surface area of this silica was determined⁶ by nitrogen adsorption and found to be 135 square meters per gram. C.P. toluene, without further treatment, was used in the swelling measurements.

SAMPLE PREPARATION

Weighed amounts of the gum rubber or the gum plus filler were sheeted out on mill rolls, and a known amount of peroxide was added. The mixture was then milled to insure thorough distribution of the peroxide. Except for the thin samples, the sheets were pressed in a four-cavity ASTM mold for 20 minutes at 125° C. This gave sheets 6 inches square and 0.080 inch thick. The procedure was to load the mold at room temperature and then put it into the heated press. The thin samples were pressed between plates using 0.040-inch shims. The press temperature and the time of pressing were the same as for thicker samples.

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When the sheets were removed from the molds, they were weighed and placed in a circulating air oven at 150° C for 24 hours. After this time, they were weighed again and the weight losses recorded. For all the samples investigated, this loss was about 9 per cent. No significant differences in weight loss were observed for samples with and without filler or with different peroxide contents.

Small samples for swelling measurements were cut from the sheets prepared as described above. These were usually about one inch long and one quarter of an inch wide.

SWELLING AND TENSION MEASUREMENTS

The small samples used in the swelling measurements were weighed and put into an excess of toluene at a temperature of 25° ($\pm 1^\circ$) C. At intervals of one or two days, each was removed and carefully placed between pieces of filter

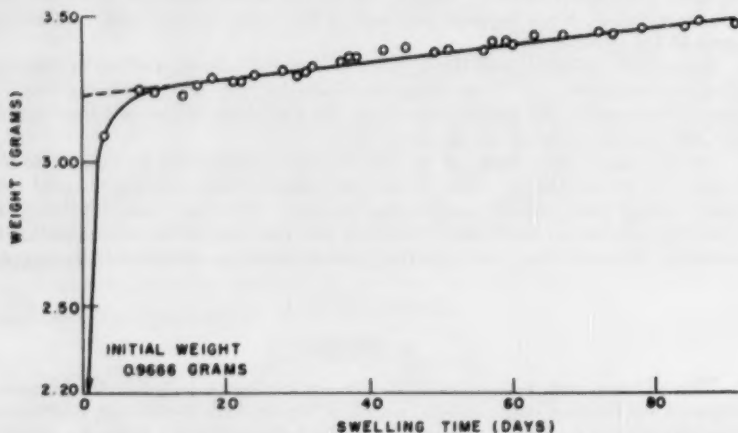


FIG. 1.—Sample weight vs. swelling time for a typical sample.

paper cut to approximately the same dimensions as the sample. By pressing the filter paper lightly against the sample, the excess toluene was blotted from the sample surface. The filter paper-swollen rubber sandwich was then placed in a closed weighing bottle and the total weight obtained. The weighing bottle was opened, the swollen rubber was removed, and the weighing bottle was quickly closed. The weight of the bottle plus wet filter paper was then determined. The difference of the two weights was taken to be the weight of the swollen rubber sample.

It was planned to continue this procedure until the swollen samples reached a constant weight. This plan had to be changed, however, because, after an initial rapid increase of weight, the samples continued to gain at a slow but definite rate. This we took as evidence of chain exchange or silanol formation, due to the presence of small amounts of potassium hydroxide or benzoic acid. An example of the type of data obtained is shown in Figure 1, in which sample weight is plotted as a function of swelling time. Since we were interested in the sample weight in the absence of this gradual change, an extrapolation back to zero time was made, as indicated, and that value used for further computations.

At the end of the experiment, the samples were placed in a vacuum desiccator and dried until they reached constant weight. The weight lost was approximately 6 per cent of the weight of the sample before the 150° C oven cure. This value seemed to be independent of peroxide or filler content.

The tension measurements were made in the conventional manner, with the samples elongated about 50 per cent. A slow stress-relaxation phenomenon was observed. This is presumably related to the slow change of swelling weight with time, described above. The tension values taken as the equilibrium ones were found by an extrapolation to zero time similar to that used in the analysis of the swelling data.

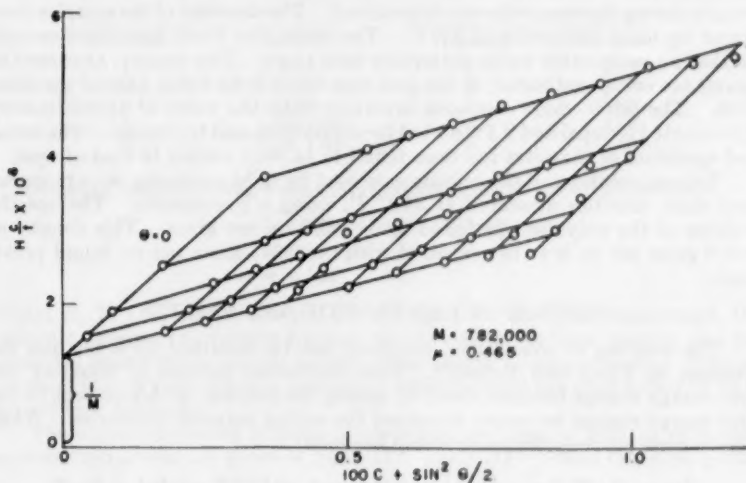


FIG. 2.—Light scattering of silicone gum in toluene.

MOLECULAR WEIGHT MEASUREMENTS

The weight-average molecular weight of the original silicone gum was obtained by light scattering in toluene. The potassium hydroxide catalyst was removed from the polymer by washing a toluene solution with dilute hydrochloric acid, precipitating with methyl alcohol, and drying the polymer in vacuum.

The light scattering measurements were made with an instrument constructed some time ago, in which the essentials were patterned after the one designed by Debye and the author⁷. The scattering cell was cylindrical, with the horn type light trap. The data obtained are plotted in Figure 2. Here H is a constant, determined by the wave length of the light used and the change in refractive index of the solution with concentration, τ is the apparent excess turbidity of the solution being investigated, c is the concentration in grams per cubic centimeter, and θ is the angle at which the scattered light was measured.

The intercept on the $H(c/\tau)$ axis has been shown to be the reciprocal of the weight-average molecular weight⁸. The slope of the extrapolated curve at $\theta = 0$ gives the second virial coefficient from which μ , the solvent-polymer inter-

action parameter, can be obtained⁹. Although μ is known to depend somewhat on concentration¹⁰, the variation will not seriously affect the results to be obtained here.

DENSITY MEASUREMENTS

The analysis of the swelling and tension data requires a knowledge of the bulk density of the polymer, the partial specific volume of the polymer in dilute toluene solutions, and the density of the filler. A series of compounds of silicone gum containing 1.65 weight per cent of benzoyl peroxide (based on gum) and different amounts of filler were prepared. They were press-cured for 20 minutes at 125° C, and given an oven cure of 24 hours at 150° C. The loss of weight during the oven cure was determined. The densities of the samples were found by water immersion at 25° C. The immersion times were short enough so that no measurable water absorption took place. The density, expressed in grams per cubic centimeter, of the gum was found to be 0.975, that of the silica 2.28. The latter value compares favorably with the value of approximately 2.2 reported for opal and 2.3 reported for crystabilite and trydimite. The infra-red spectrum of the silica has been found to be very similar to that of opal.

Toluene solutions of the silicone gum used for light scattering were prepared and their densities measured at 34.4° C, using a pycnometer. The specific volume of the polymer was found to be 1.022 cc. per gram. This density of 0.978 gram per cc. is to be compared with the 0.975 gram per cc. found previously.

METHOD OF CALCULATION AND RESULTS

The swelling of cross-linked polymers can be described by a relation developed by Flory and Rehner¹¹. Their derivation consists of equating the free energy change brought about by mixing the polymer with a solvent to the free energy change necessary to extend the coiling polymer molecules. When this is done properly the relationship becomes:

$$[c_0 - (1/M)] = - [\ln (1 - v_2) + v_2 + \mu v_2^2] / 2V_1\rho(v_2^{1/3} - 2v_2/3)$$

where c_0 is the apparent number of moles of cross-links added to a gram of polymer having a bulk density of ρ and a number-average molecular weight of M before cross-linking. The quantity v_2 is the volume fraction of polymer in the sample which has reached its equilibrium swollen state after being immersed in a swelling agent having molar volume of V_1 . The functionality of the cross-

TABLE I
VALUES OF PARAMETERS FOR SWELLING EVALUATION

$M = 391,000$	$f = 4$
$\mu = 0.465$	$V_1 = 107.0$
$\rho = 0.978$	$v_0 = 0.85$

links in the sample is given by f ; the solvent-polymer interaction parameter μ is the same as that in the Flory-Huggins theory of polymer solutions. If the polymer has been cross-linked in the presence of a diluent, a correction must be applied in the form given by $v_0^{1/3}$ in the above expression; v_0 is the volume fraction of polymer in the diluent-polymer mixture at the time of cross-linking. This must be taken into account in our case, since an appreciable amount of material was removed from the sample during the oven curing and swelling processes.

The molecular weight called for in the above expression is the number-average, while we have measured the weight-average. For a "normal" distribution type of polymer, the weight-average molecular weight is the larger by a factor or two. A rough fractionation led to a factor of 1.8. For purposes of calculation, we shall assume that this factor of two is applicable in our case.

Table I gives a résumé of the values of the parameters used in the above equation for the analysis of the swelling data.

TABLE II
NUMBER OF CROSS-LINKS PER GRAM OF SILICONE GUM FROM
SWELLING MEASUREMENTS

Thick samples		Thin samples	
% peroxide	$c_0 \times 10^3$	% peroxide	$c_0 \times 10^3$
1	0.94	1	1.44
2	1.35	2	2.13
3	1.70	3	2.69
4	1.85, 1.89	4	2.82
5	1.94, 1.93	5	3.49

The tension measurements were analyzed according to the relationship:

$$\tau = 2RT\rho v_2' [c_0 - (1/M)]\varphi(\alpha)$$

$$\varphi(\alpha) = \alpha - 1/\alpha^2$$

$$\alpha = L/L_0$$

where R , T , ρ , v_2' and L are the gas constant, the absolute temperature, the polymer density, the volume fraction of polymer in the filled sample, and the extended length of the sample having initial length L_0 , respectively. This expression is to replace the one previously derived which has been found to be in error¹² (see Appendix).

The apparent number of moles of cross-links per gram of gum, c_0 , computed as described above, are given in Table II. Table III contains the same quant-

TABLE III
NUMBER OF CROSS-LINKS PER GRAM OF GUM IN SILICONE-SILICA
COMPOUNDS

81.7% silicone			89.8% silicone		
% peroxide	$c_0 \times 10^3$		% peroxide	$c_0 \times 10^3$	
	swelling	tension		swelling	tension
1	5.1	6.0	0.98	3.8	4.0
2	8.0	7.8	1.97	5.5	5.1
3	9.9	9.8	2.95	6.2	5.9
4	10.8	11.1	3.94	6.4	6.1
5	11.4	12.6	4.92	6.7	7.0

ity for the samples with filler added. The data are represented graphically in Figures 3 and 4. Both the number of cross-links and the amount of peroxide are based on the gum content of the samples. The percentages of silicone gum in each series after heating, swelling, and drying are shown in Table III; the remainder of the samples is silica. The peroxide percentages quoted are those initially present in the sample before curing.

Apparent efficiencies for the formation of cross-links by benzoyl peroxide may now be computed. This has been done, using the data in Tables II and

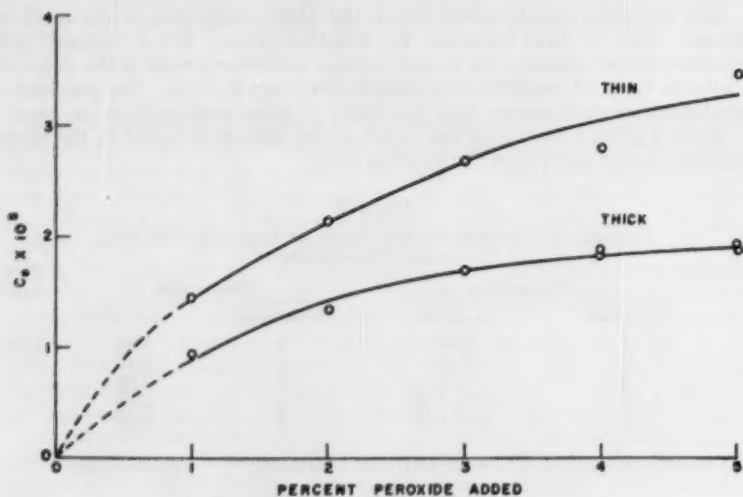


FIG. 3.—Moles of cross-links vs. peroxide concentration in silicone gum.

III and the assumption that, if the process were 100 per cent efficient, one mole of peroxide would produce one mole of cross-links. The results of the computations are shown in Figures 5 and 6. It will be observed in Figure 6 that the sample containing 81.7 per cent silicone gum gives an efficiency value of over 100 per cent. This anomaly will be discussed later.

$$M = 391,000$$

$$\mu = 0.465$$

$$\rho = 0.978$$

$$f = 4$$

$$V_1 = 107.0$$

$$v_0 = 0.85$$

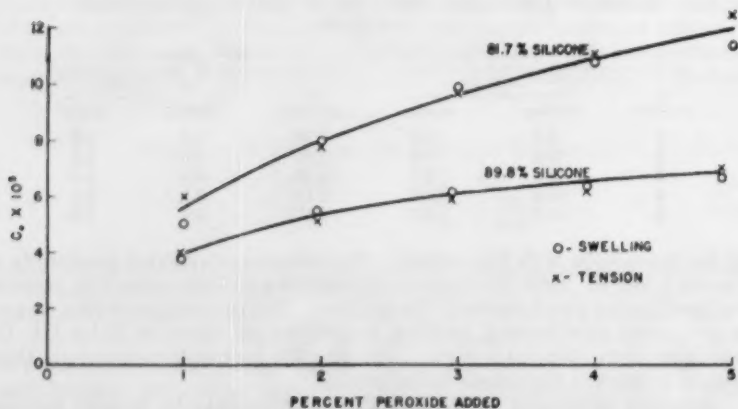


FIG. 4.—Moles of cross-links vs. peroxide concentration in silica-silicone compounds.

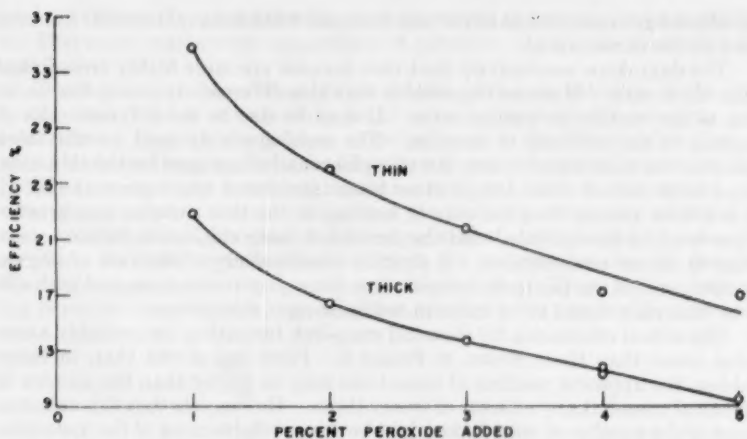


FIG. 5.—Apparent efficiency for cross-link formation by benzoyl peroxide in silicone gum.

DISCUSSION

The data in Figures 3 and 5 show that the efficiency of cross-link formation in silicone gum decreases markedly as the peroxide concentration is increased. The maximum number of moles of cross-links per gram of gum appears to be about 2 to 4×10^{-5} for the thick and thin samples, respectively. This corresponds to a minimum average of 680 to 340 siloxane units between cross-links under these conditions of curing. Such a sample is very loosely cross-linked, compared with other elastomers. It is not surprising, then, that a high-modu-

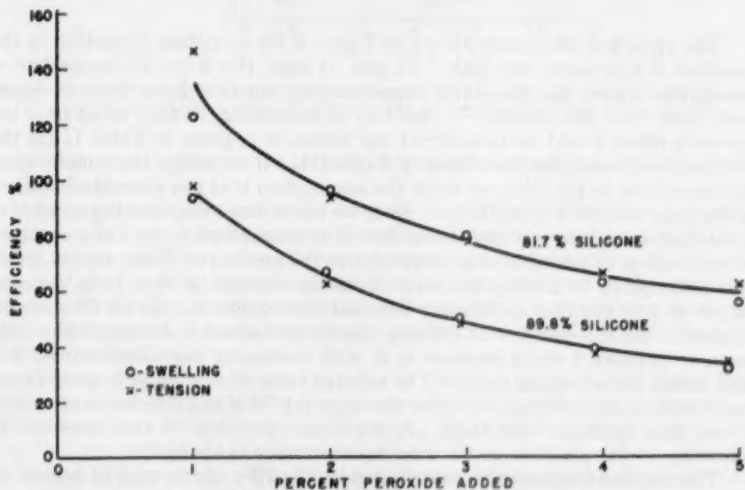


FIG. 6.—Apparent efficiency for cross-link formation by benzoyl peroxide in silicone-silica compounds.

lus silicone gum sample has never been reported when benzoyl peroxide has been used as the curing agent.

The data show conclusively that thin samples are more highly cross-linked than thick ones. It seems improbable that this difference is due to the variation of the surface to volume ratio. It may be due to the different rates of heating of the two sets of samples. The mold assembly used for the thick samples was more massive than the thin plates and shims used for the thin ones. Since both were at room temperature when introduced into a press at 125° C, it is almost certain that the rate of heating of the thin samples was greater. Thus it might be concluded that the peroxide is more efficient in forming cross-links at higher temperatures. A detailed kinetic study of the rate of decomposition and of the products formed when benzoyl peroxide is heated with silicone materials would be of value in determining if this is true.

The actual efficiencies for chemical cross-link formation are probably somewhat lower than those shown in Figure 5. Flory has shown that, in Butyl rubber, the apparent number of cross-links may be higher than the number of chemical cross-links by a factor of two or three. He suggests that this enhancement of the number of cross-links might be due to intertwining of the molecules. While this intertwining for silicones may not be as great as that in Butyl rubber, it seems probable that the effect still exists.

TABLE IV
RATIO (*R*) OF CROSS-LINKS ASSIGNED TO 18.3 AND 10.2 PER CENT FILLER

% peroxide	<i>R</i>
1	1.3-1.9
2	1.5-1.8
3	1.8-2.0
4	2.0-2.2
5	1.9-2.2
Average	1.86

The apparent efficiencies shown in Figure 6 for cross-link formation in the presence of filler seem very high. In part, at least, this is due to the method of calculation where the cross-links introduced by the filler have been included with those from the peroxide¹². One way of separating the filler effect from the peroxide effect would be to subtract the values of c_0 given in Table II for the thick peroxide samples from those in Table III. If we assign the remainder of the cross-links to the filler, we make the assumption that the peroxide efficiency is the same with or without filler. Since we know, however, that the number of cross-links introduced by the filler at low filler concentrations and at a constant concentration of peroxide is proportional to the amount of filler, we can check this assumption by finding the ratio, *R*, of the number of cross-links assigned in this way to the filler for the two different filler contents. Table IV contains this ratio for the samples of different peroxide content. Although the data seem to indicate a slight increase in *R* with increasing peroxide content, it is well within experimental error. The average ratio, *R* = 1.86, is in good agreement with that to be expected from the ratio of 1.79 of the filler concentrations. These data indicate that there are no large variations of the cross-linking efficiency of the peroxide as the filler concentration is changed.

The number of cross-links contributed by the filler can be seen to depend on the amount of peroxide added by an examination of Figure 4. Since we have found that the peroxide efficiency seems essentially the same for different filler

concentrations, the curves of c_0 vs. peroxide would be expected to be parallel if the filler contribution were independent of peroxide. This is far from being the case.

The dependence on peroxide concentration of the contribution of the filler to the total number of cross-links might be expected from the following considerations. Suppose the polymer attached itself to the filler so that loops of polymer chains dangling from the filler surface were of varying lengths. This could come about by a random attachment of molecules to the surface. A somewhat similar situation could arise if the molecules were only attached at their ends whereas the original polymer consisted of a distribution of molecular weights. As more cross-links are added to the system, the chances that the shorter loops are cross-linked to the network increase. Thus, with an increasing peroxide concentration, one might expect that the number of cross-links

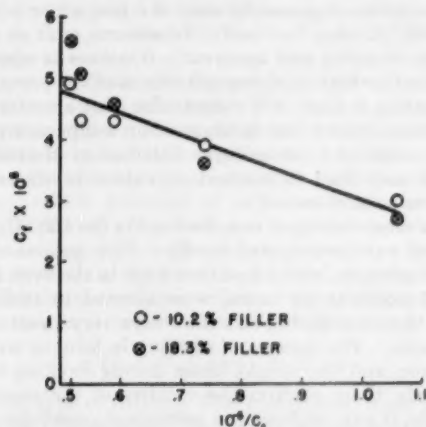


Fig. 7.—Apparent number of moles of cross-links contributed by the filler vs. reciprocal of the cross-links introduced by the peroxide (the values for 18.3 per cent filler have been divided by 1.79).

contributed by the filler would increase. This is the general behavior illustrated in Figure 4.

An approximate treatment for samples very dilute in filler (see Appendix) suggests that the data be treated according to the relationship $c_f = N_0(\alpha' - \beta/c_0)$, where c_f is the number of moles of cross-links contributed by the filler per gram of gum, c_0 is the number of cross-links per gram of gum in the absence of those from the filler, α' and β are constants for a given polymer-filler system, and N_0 is the number of moles of polymer, per gram of gum, that have been adsorbed on the filler.

The concentration of cross-links due to the filler, c_f , have been found from the data of Table III by subtracting the c_0 values for the thick peroxide samples. These have been plotted vs. $1/c_0$ in Figure 7. The data for the samples containing 18.5 per cent filler have been divided by 1.79, so they should coincide with those for 10.2 per cent. The data are not extensive enough to decide whether the system investigated is in complete agreement with the model. They do, however, point out that the contribution of cross-links by the filler depends on

the degree of cross-linking of the sample. In these experiments c_f changes by a factor of 1.7 for a two-fold variation in cross-link concentration.

It seems interesting to evaluate the constants α' and β and relate their values to the parameters used in the model for the system. This has been done and the value of 33 Å. has been obtained from the intercept at $c_0^{-1} = 0$ for the area per molecular attachment¹³. An analysis of the slope of the line as drawn in Figure 7 leads to a value of 44,700 for the number-average molecular weight of the loops.

Since the above values are approximately of the expected order of magnitude, it is tempting to say that the model represents the actual system fairly well. However, because the decomposition products from the peroxide may influence the nature and number of the polymer-filler attachments, such a conclusion is not justified on the basis of these data alone.

A few qualitative experiments with benzoyl peroxide in silicones have been conducted. The peroxide generally used is a fine white powder that melts in the range 105–106° C when by itself. In silicone gum at a concentration of about 2 per cent, it melts, and apparently dissolves at about 45° C. At this moment there must be high local concentrations of the peroxide in the polymer. If the rate of heating is high, it is conceivable that a uniform distribution has not been established before the decomposition temperature is reached. This would probably result in a nonuniform distribution of cross-links throughout the sample, and may lead to marked curvature in stress-relaxation plots¹⁴. Such an effect has been observed.

The degree of cross-linking of samples kept in the 150° C circulating air oven for varying times was investigated briefly. Five gum samples, cured with 2 per cent benzoyl peroxide, which had been kept in the oven for a period of time ranging from 17 hours to 94 hours, were allowed to swell in toluene. The weight losses in the oven during this time were very small and all of the same order of magnitude. The degrees of swelling in toluene were identical within experimental error, and the weight losses during swelling also were identical. These experiments, then, confirm the validity of the usual assumption that there will be little, if any, stiffening or additional crosslinking of polydimethylsiloxanes during such a treatment.

APPENDIX

The experimental results have been analyzed with the implicit assumption that the kinetic theory of rubber elasticity is valid. This requires that the major portion of the force of retraction in the tension experiments, for example, arises because of the changes in configurational entropy when the samples are elongated. The enthalpy changes must be small. Experiments on other elastomers have shown that, in some instances, this is a reasonable approximation¹⁵. On this basis and from the results of preliminary experiments on polydimethylsiloxanes, it seems that the use of the kinetic theory is justified in the absence of filler and at low elongation.

In the presence of filler, however, the situation becomes more complex. The incorporation of the filler into the gum rubber is undoubtedly accompanied by an appreciable enthalpy change. Fortunately, our method of investigation involves only the free energy changes on deforming the sample, and is not primarily concerned with the process of mixing polymer and filler. Using it assumes that, even in the presence of the filler, the enthalpy contributions are small compared with those due to entropy changes. There is evidence that

this is true in some other polymer-filler mixtures¹⁶. The close agreement between the swelling and tension results might be taken as support for this assumption in the present case. It seems unlikely that if there is a major enthalpy change, it would contribute equally to measurements both in the presence and absence of the swelling liquid.

The kinetic theory result¹⁵ that the tension, τ , in a sample is given by:

$$\tau = 2kTv\varphi(\alpha) \quad (1)$$

will now be examined in some detail for the instances where filler is present. Here k is Boltzmann's constant, T is the absolute temperature, v is the number of circuitous paths per unit volume of polymer discussed by Flory¹⁷, and:

$$\begin{aligned} \varphi(\alpha) &= \alpha - 1/\alpha^2 \\ \alpha &= L/L_0 \end{aligned}$$

where L is the stretched length of the sample having an initial length L_0 . Following the scheme of Flory, we shall start with N primary polymer molecules and, by adding chemical cross-links, tie them into a single structure. Before we do this, however, we shall mix with the polymer n filler particles each having m sites on which polymer can be adsorbed. The number of circuitous paths we have in the final system will depend on how we let the polymer be adsorbed. For purposes of illustration, we limit ourselves to two simple cases.

We first consider the case in which each filler particle adsorbs m polymer molecules; each molecule is adsorbed at only one point along the molecule. The sample then consists of $(N - nm)$ free polymer molecules and n filler particles, to which nm polymer molecules are attached. We need $N - nm + n - 1$ chemical cross-links to tie this material together into one large structure. Each additional cross-link will form one additional circuitous path. Thus, if x is the number or cross-links in a unit volume of polymer:

$$v = (x - N + nm - n + 1.)$$

It is obvious that this type of polymer-filler attachment leads us to expect that the contribution to the tension of the filler would be independent of the chemical cross-link content, provided enough cross-links are present to form a network.

Next we consider the case in which each adsorbed polymer molecule is attached to the filler at two sites. This results in polymeric loops on the surface of the filler. There will be $nm/2$ polymer molecules adsorbed and $N - (nm/2)$ free polymer molecules in the system. To connect all of the material into a single structure will require $N - (nm/2) + n - 1$ chemical cross-links. The effect of additional cross-links will now depend specifically on where they enter our system. If a cross-link is formed between polymer not directly attached to the filler, only one additional circuitous path is formed. If a cross-link is formed between a loop and polymer not directly attached to the filler, two additional circuitous paths are formed. Likewise a cross-link between two loops on different filler particles results in three additional circuitous paths. Once a loop has been crosslinked to the rest of the system, additional cross-links produce only one circuitous path.

To gain an estimate of this effect, we shall now consider a polymer-filler system so dilute in filler that the chance for the interaction of filler particles is small and can be neglected. We shall also neglect some of the effects of cross-links of one loop to another in that we shall assume that, if a loop does contain a cross-link, it will contribute two circuitous paths.

Thus in adding x cross-links, we obtain a number of circuitous paths equal to:

$$\nu = x - N + (nm/2) - n + 1 + (nm/2)F(\xi, x)$$

where $F(\xi, x)$ is a function of the number, ξ , of loops having i polymer structural units, and the number of cross-links. If all of the loops are cross-linked to the rest of the system, $F(\xi, x) = 1$ and, if none are cross-linked, it is zero.

The exact form of the function $F(\xi, x)$ depends on the distribution of loop sizes. Although an estimate of this size distribution has been calculated for the case of adsorption of polymer from dilute solution, there seems to be no reported treatment applicable to the present case¹⁰. Bearing in mind that other distributions may be more correct, we shall assume one which gives us a simple answer for comparison with the data at hand. When the subject of polymer adsorption is understood in greater detail, the present treatment can be modified.

Consider the special case in which the probability of having a loop of i units is ξ and is independent of loop size from $1 \leq i \leq p$. For values of $i > p$, this probability is zero. Since the total number of loops must equal $nm/2$, the value of ξ is $nm/2p$. Let ϵ denote the volume of a single polymer structural unit capable of being cross-linked. To find the number, Q , of loops cross-linked at least once, we must add up the contributions from loops of all sizes:

$$Q = \frac{nm}{2p} - \frac{nm}{2p} \sum_{i=1}^p (1 - \epsilon x)^i$$

So:

$$F \cong [1 + 1/p - 1/p\epsilon x]$$

The total number of circuitory paths becomes approximately:

$$\nu = x - N + (nm/2)(1 + F)$$

where unity has been neglected with respect to N and $m/2$.

The presence of the filler makes necessary one other modification of Equation (1). Since we normally wish to compute the tension, τ , in terms of the actual dimensions of the sample, and since we have expressed ν in terms of the volume of the polymer in the sample, we must multiply ν by v_1 , the volume fraction of polymer.

It was pointed out by S. Baxter that $\varphi(\alpha)$ does not need the modification previously given¹². He called attention to the fact that it can be shown simply that a line passing through a sample containing a volume fraction of filler v_2 will have a fraction v_2 of its length within filler particles. Since, on stretching, the sample v_2 remains constant, the ratio L/L_0 is independent of v_2 to the approximation employed here¹³.

Equation (1) then becomes:

$$\tau = 2kTv_1 [x - N + (nm/2)(1 + F)]\varphi(\alpha)$$

where $\varphi(\alpha)$ is identical to that given before. If we let r denote the radius of spherical filler particles and f the number of attachments per unit area, the expression can be written as:

$$\tau = 2RTv_1 \left[c - \frac{\rho_1}{M} + \frac{3f}{2Ar} \frac{v_2}{v_1} (1 + F) \right] \varphi(\alpha)$$

where we have shifted to molar quantities and R is the gas constant, c is the moles of cross-links per unit volume of polymer, ρ_1 and M are the polymer density and molecular weight, and A is Avogadro's number. On the same basis:

$$F \cong \left[1 + \frac{\rho_1 A \epsilon}{M_1} - \frac{\rho_1}{M_{1c}} \right]$$

where M_1 is the maximum molecular weight per loop. In many high polymer systems we would expect the second term to be small compared to unity. In such a case:

$$F \cong 1 - \rho_1/M_{1c}$$

SYNOPSIS

The formation of cross-links in silicone rubber by benzoyl peroxide was studied by tension and swelling techniques as a function of curing conditions and filler content. The ability of benzoyl peroxide to form cross-links was found to decrease markedly as the peroxide concentration was increased. The peroxide seems to form cross-links in an amount independent of the concentration of the silica filler. High cross-link concentrations were found to be necessary to fully utilize the polymer-filler attachments. Values for the bulk and solution densities of silicone gum and the specific volume of the filler in silicones were determined. The melting point of benzoyl peroxide immersed in silicone gum is reported. The aging of silicone gum at 150° C in air was found to neither increase nor decrease the number of cross-links.

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PERFORMANCE OF CARBON BLACKS

INFLUENCE OF SURFACE ROUGHNESS AND POROSITY *

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The relationship between surface area and particle size of a pigment is a very simple one when it is assumed in first approximation that the pigment consists of spheres of the same size. In 1 gram of pigment there are $\frac{1}{4/3 \pi R^3 \times S}$ spheres, where S = specific gravity. Each sphere has a surface of $4\pi R^2$, so that the total surface in 1 gram of pigment is:

$$\frac{1}{4/3 \pi R^3 S} \times 4\pi R^2 = \frac{3}{RS} \text{ or } \frac{6}{DS}$$

For carbon black, $S = 1.85$, so that the formula becomes $SA = \frac{3.2}{D}$ and, if D is expressed in millimicrons (10^{-7} cm.) and the surface area in square meters per gram:

$$SA = \frac{3200}{D}$$

so surface area is inversely proportional to the diameter of the particle. For an EPC black with an average particle diameter of 32 m μ , surface area would become exactly 100 square meters per gram. This is approximately what is found for an EPC black.

PRACTICAL METHODS FOR DETERMINING SURFACE AREA AND PARTICLE SIZE

Direct observation of channel and furnace types of carbon blacks under the electron microscope has shown that they are composed of essentially spherical particles fused together into chainlike aggregates, which are further clustered together into loose agglomerates. By counting the spherical particles of various sizes, the familiar curve of distribution of sizes around the average may be constructed. Because the smaller particles contribute less to the weight than the larger particles, the weight average will be more to the side of the larger diameters and a similar consideration holds for the average necessary for computing the surface area. If the particles are assumed to be perfect spheres, the area of fusion to be negligible, and the counting to be unbiased, the average can be calculated exactly¹, to arrive at a correct surface area from electron microscope countings².

The second method of determining the surface area of a pigment makes use of measurements of adsorption. These adsorption determinations are mostly

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made with nitrogen at low temperatures, and are almost a standard test in laboratories working with finely divided pigments. The method is based on the detection of the formation of a monolayer of nitrogen on the particle surface and the dimensions of the nitrogen molecule in this monolayer³. Although well reproducible, the adsorption method also involves a number of assumptions about the coverage area of the nitrogen molecule and the significance of the inflection point on the adsorption isotherm as the point of monolayer coverage.

Notwithstanding the various sources of error in both the electron microscope counting and the adsorption method, a remarkably close correlation has been obtained between the surface area values from both methods for many commercially available blacks. In a number of cases, the adsorption surface areas are considerably higher than those found by electron microscope counting.

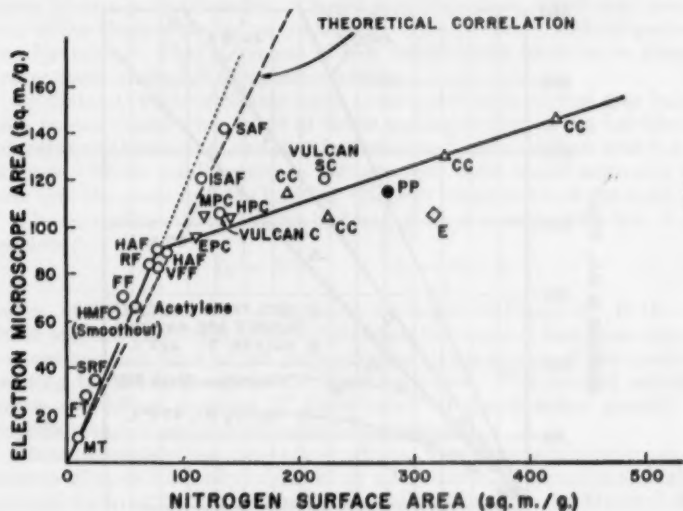


FIG. 1.—Surface area correlation.

The differences may be as large as a factor 4 or 5. Blacks that show this phenomenon are the channel black of very fine particle size, aftertreated, long-flow-ink blacks, and the more recent conductive furnace blacks like Vulcan-C and Vulcan-SC. The correlation between the surface areas measured according to the two methods is shown² in Figure 1, which illustrates the much larger adsorption surface area found for some of the finer types of black. This effect is ascribed to porosity, and a "roughness" or "porosity" factor, f , may be defined as⁴:

$$f = \frac{\text{adsorption surface area}}{\text{electron microscope surface area}}$$

The surface characteristics of a type of black may be changed considerably by oxidation. It is very interesting to follow the change of surface area as a function of the loss of weight of a certain black caused by oxidation and removal of the oxidation product. Apparently a carbon black particle does not burn

uniformly on its outer surface, decreasing in particle size and giving rise to the normal geometric increase in surface area. On the contrary, the carbon black particles appear to burn preferentially at certain surface sites, opening up pores and crevices and providing internal surface area available for adsorption of nitrogen molecules, without changing appreciably the particle size, as observed under the electron microscope.

This effect of large increases of surface area, with insignificant changes of particle diameter, is particularly noticeable for the so-called "after-treated" or oxidized channel blacks which are produced for the ink and lacquer industries. These blacks are produced by air oxidation in open treating troughs, which are directly heated by open gas flames. The increase of surface area due to a homogeneous reduction of the particle size because of oxidation of the outer

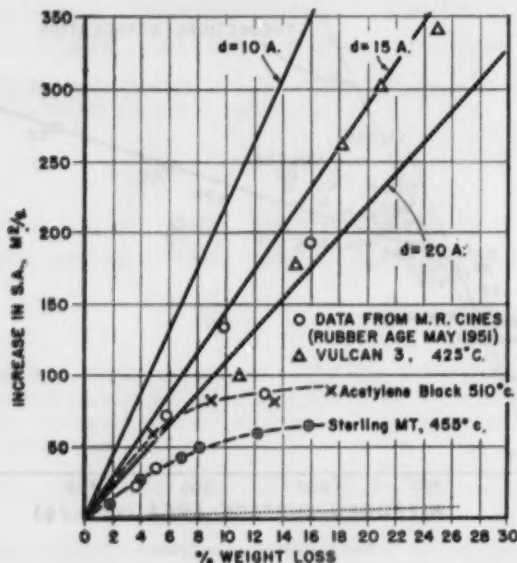


FIG. 2.—Relation of increase of surface area to oxidative weight loss for different pore diameters.

shell may be plotted against the computed loss in weight. For the model black with $D = 32 \mu$ and $SA = 100$ square meters per gram, a loss of weight of 25 per cent by removal of the outer shells of particles would reduce the diameter of the particles by only approximately 7 per cent and increase the surface area by only 7 per cent or 7 square meters per gram (Figure 2). Actually, in practice, for a loss of weight of about only 7 per cent, an increase of surface area of as much as 150 square meters per gram may be obtained⁵. This must be an internal surface due to deviations of the shape of the particle from the spherical form and, in the extreme case, the particle may become porous like a sponge. Assuming these pores to have cylindrical shape of infinite length and a constant diameter, the loss of weight and the increase of surface area accompanying the formation of these pores can be computed according to the formula:

$$\Delta(SA) = \frac{4}{1.85D} \text{ weight loss}$$

Figure 2 illustrates the idealized development of surface of the model particle by formation of cylindrical pores of various diameters.

CHARACTERISTICS OF BLACKS WITH INCREASING SURFACE AREA

If a black of the HAF type, for instance, is oxidized in a slow stream of air under proper precautions in a tubular laboratory oven at about 400° to 450° C (750° to 840° F) and devolatilized afterward at about 900° C (1650° F), the surface area is increased and some weight is lost. Plotted in Figure 2, many of the points are near the line indicating formation of 15 Å. pores. This means an increase of surface area of approximately 15 square meters per per cent loss in weight. If the oxidation is carried out at too high a temperature, the measured points deviate in the direction of larger pore diameters, which may mean that some of the black is burned on the outside of the particles, without preferential pore formation. That a process of this nature must have taken place finds further proof in the following observations.

Preliminary work⁶ indicates much lower adsorption surface area values for these porous blacks when gases of larger molecular dimensions [dichlorotetrafluoroethane (Freon-114) and decafluorobutane] are used than with the use of nitrogen. These results seem to indicate that these larger molecules cannot enter into the pores and the limiting diameter seems to be on the order of 15 Å.

The crystallites that form the building units of each particle are of the dimensions:

$$L_a = 24 \text{ Å.} \quad L_c = 13.1 \text{ Å.}$$

that is, of the same order as the pores envisaged in Figure 2. If the oxygen attack starts at the edges of the crystallites, burning out first those crystallites that are oriented more or less perpendicular to the surface of the particle, the resulting holes will resemble the idealized pores. The rate of oxidation of carbon crystallites is about 17 times faster in the direction parallel to the graphite planes than perpendicular to the planes⁷.

Measurements of the dielectric loss factor over a range of frequencies of dispersions of these blacks in rubber show a maximum which shifts to higher frequencies for blacks of higher surface area. According to the Maxwell-Wagner theory, this is due to a lower effective dielectric constant, which can be explained only by porosity. An idealized picture of the result of the oxygen attack is given in Figure 3.

Porosity is not only obtained by aftertreating the separated black in the laboratory; some aftertreatment may be part of the production process so that blacks of a considerable porosity may be produced in one manufacturing operation.

POROSITY OF BLACKS PRODUCED DIRECTLY IN FURNACE

The normal commercial rubber grades of oil furnace blacks are essentially nonporous and have relatively small variations in surface areas of nitrogen adsorption. On the other hand, it is possible to change production conditions, furnace designs, and raw materials so as to produce wide surface area changes without changing the ultimate particle size of the products.

Table I gives data taken from a wide variety of studies made during pilot-plant investigations. In the first column is listed the type of black to which the particle sizes of these experimental blacks most nearly correspond, in the order of decreasing particle size. In the next column is listed the Cabot

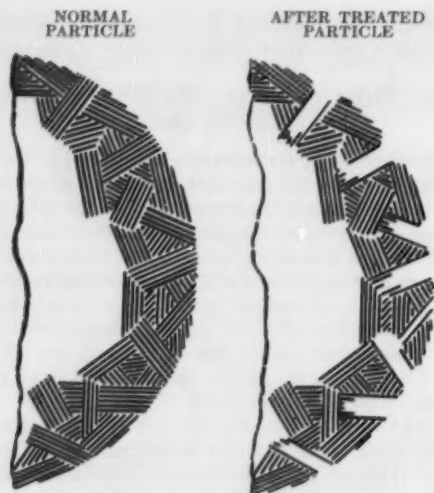


FIG. 3.—Effect of oxidation on carbon black particles.

Nigrometer scale range for each type. This scale value is a measure of blackness or jetness and gives a reliable indication of particle size; the higher the scale value, the less black or jet is the sample, and the larger is the particle size. The scale ranges shown are very small, between 1 and 2 scale points, and the variation of particle size corresponding to this few-point spread could hardly be detected on electron microscope examination. The tinting strength values are also related to particle size, with high values corresponding to small particle size. Tinting strength values, as can be seen, serve to classify these blacks into the various types, since there is practically no overlapping of one range into the other. In the last column are listed the surface area ranges which have been observed in the normal course of pilot plant development. The values shown are determined by iodine adsorption from solution, a method which has been empirically correlated with the low temperature nitrogen-adsorption method, and which is in constant use in these control and development laboratories. It is evident that any particular type or grade of carbon black can be produced, directly in the furnace, with a wide range in surface area and essentially constant particle size.

Although numerous studies have been published on carbon black particle size, pH, and structure, there is no reported work on the effect of particle

TABLE I
ANALYTICAL DATA OF OIL FURNACE BLACKS OF FINE PARTICLE SIZE

Black type	Nigrometer scale range	Tinting strength range	Surface area from electron microscope (sq. m./g.)	Number av. diameter (dn, mμ)	Iodine adsorption surface area (sq. m./g.)
FEF	94-95	113-138	63	30	28-199
HAF	89-90	166-188	74	24	52-104
I-SAF	86-87	215-244	121	16	84-186
SAF	82-84	238-260	142	14	83-151

porosity on performance in rubber. The present investigation, using experimental carbon blacks covering extreme ranges of surface area at constant particle size, has shown that porosity gives rise to three noticeable effects in rubber. A most pronounced effect of high surface area is a retardation in the rate of vulcanization. Another vulcanizate property affected by porosity is resilience, which shows a slight, but noticeable decrease with increasing area. The electrical conductivity imparted to rubber by carbon black is sharply increased by the extension of surface area. The particle size has been unchanged in these studies.

Retardation of Cure.—Carbon blacks, particularly the acidic channel blacks, tend to retard the rate of vulcanization. This is observed if the carbon black compound is compared with a pure-gum compound in respect to the rate of cure

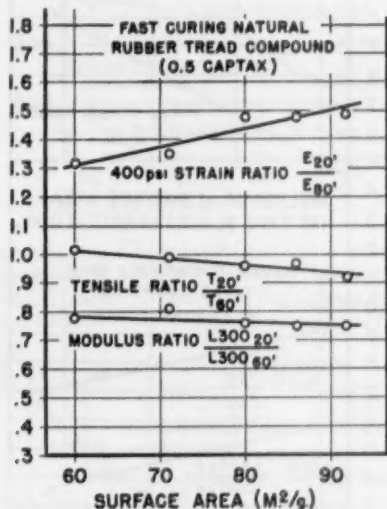


Fig. 4.—Influence of surface area of HAF-type blacks on rate of cure.

in the technological sense, i.e., vulcanization time necessary to develop optimum properties. It has been suggested that carbon black interferes with the curing mechanism by physically adsorbing the compound curatives and so removing them from the field of activity in the rubber matrix. Thus, the rubber matrix has less than the added amounts of accelerator, sulfur, or curing intermediates, which results in a slowing down of cure rate. Increasing surface area should aggravate the condition of curative adsorption, and this effect is shown in Figures 4 to 6.

For this work, a series of HAF-type blacks was chosen, covering a rather small range of surface areas; even this range is not typical of present commercial HAF grades, which have a somewhat narrower range. These blacks are all essentially equivalent in their reinforcing abilities when compared in the laboratory at optimum cures. The effect on cure rate is shown by plotting the tensile strength and modulus ratios for the 20- and 60-minute cures. The NBS strain ratios have been taken for the 20- and 80-minute cures. For the compound

shown in Figure 4, it is evident that the range of surface areas taken has very little influence on cure rate. It may be concluded that this compound has more than an adequate amount of curatives and is, therefore, rather insensitive to the curative adsorption of the increased surface area.

Figure 5 shows the same series of blacks in a slower curing cold GR-S tread compound. In this case, the slower curing nature of the compound is evident from the lower levels of the tensile and modulus ratios and the higher level of the strain ratio. The more pronounced slope of the lines indicates a noticeable sensitivity to curative adsorption caused by increased surface area. Thus, in a compound that is already relatively slow curing, curative adsorption differences over the range of surface areas shown have a noticeable effect on curing rate.

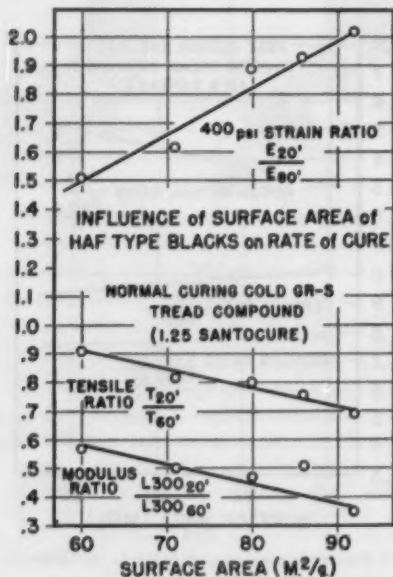


FIG. 5.

In Figure 6, a purposely underaccelerated cold GR-S tread compound is shown. This compound is extremely sensitive to the small quantity of tetramethylthiuram disulfide (Tuads) used, and gives much superior properties if the tetramethylthiuram disulfide is increased to 0.15 to 0.20 part. Using 0.125 part, no cure could be obtained in 20 minutes, so that the properties for the 80-minute cures are shown on the figure rather than the property ratios. The low level of tensile strengths and the tensile variation with surface area are very pronounced. This series of figures demonstrates that the effect of carbon blacks on curing rates is very dependent on the particular compounds used, and that differences in curing behavior due to surface area can be minimized by compound adjustments.

Effect of Internal Surface Area on Rebound Resilience.—Figure 7 shows the relationships of rebound resilience to surface area for two different particle size

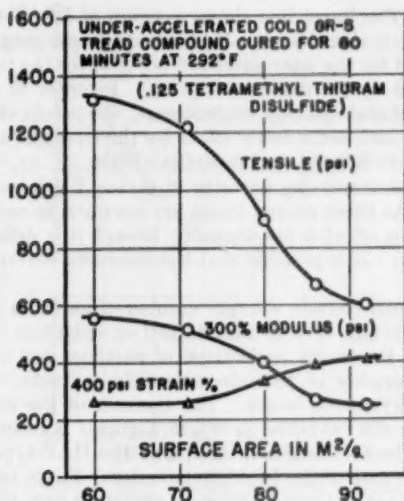


FIG. 6.—Effect of surface area of HAF-type blacks on cure.

grades of oil furnace blacks. The rebound resilience in both cases is expressed in percentage of a standard HAF black control. The upper line for a group of HAF-type experimental blacks (Nigrometer scale range 89 to 90) shows a variation of only 5 per cent for the two-fold range of surface area of 50 to 100 square

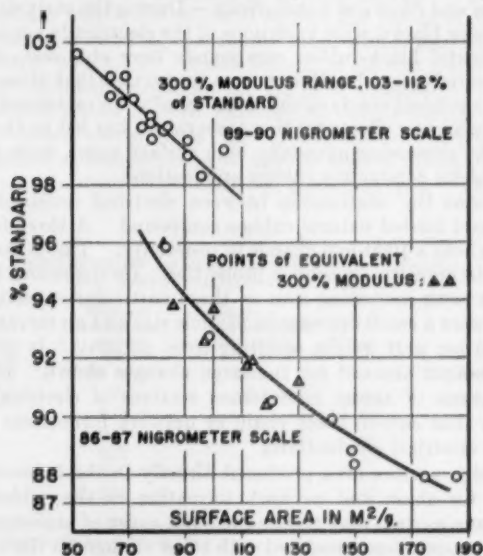


FIG. 7.—Relation of rebound to surface area of cold-rubber compounds.

meters per gram. The lower line shows a group of I-SAF-type experimental blacks of finer particle size than the HAF blacks (scale range 86 to 87). The variation of rebound for the later series is 6 per cent for the two-fold increase of surface of 90 to 180 square meters per gram. In order to avoid as much as possible the effect of state of cure on resilience, the points shown in the upper curve by the circles and in the lower curve by the triangles are for cures which gave essentially equal 300 per cent modulus-values.

It is evident that increasing porosity of carbon black gives rise to greater hysteresis losses. As these energy losses are assumed to occur at the carbon-rubber interface, this effect is not amazing, though it is difficult to visualize a detailed mechanism. It is possible that the increased surface roughness plays a part in this case.

Porous blacks must contain a larger number of particles per unit weight, if constancy of particle size is to be maintained on oxidation. At equal weight loadings in rubber, the larger population of particles per unit volume would result in a larger number of particle-to-particle contacts, which may give a consequent rise in hysteresis losses. The increase of the number of particles per unit volume for the examples shown in Figure 7 is estimated to be only 4 per cent for the highest surface area sample of the HAF-type series, and 8 per cent for the extreme case of the I-SAF-type series. These values are about the same as the percentage changes in rebound resilience over the range of surface areas shown.

Studies of electrical conductivity, using porous blacks, indicate the possibility that porosity decreases the ability of the carbon agglomerates to be dispersed. This effect of network formation in rubber by porous carbon blacks could cause greater hysteresis losses because of the increased possibility of particle-to-particle friction.

Surface Area and Electrical Conductivity.—During the early days of development of oil furnace blacks, wide variations of the electrically conductive properties of experimental black-rubber compounds were obtained, although other properties appeared normal. It was soon recognized that those blacks which imparted high electrical conductivity were usually characterized by higher adsorption surface areas. Recently this observation has led to the development of carbon blacks possessing unusually high surface areas, so as to make them especially useful for conductive rubber applications.

Figure 8 shows the relationship between electrical resistivity and surface area for a 50-part loaded natural rubber compound. A three-fold increase of area results in about a 1000-fold change in resistivity. This is the most striking effect of particle porosity on rubber properties. Contributing to the increase of conductivity with increasing area of these particular experimental furnace black samples were a small decrease in particle size and an increase in the number of particles per unit weight resulting from porosity. It is felt that both these factors cannot account for the large changes shown. Electron microscope examinations of actual microtomed sections of electrically conductive stocks indicate that carbon black chain or network formations are associated with increased electrical conductivity.

Blacks of high surface area produced directly in the furnace must possess this tendency for chain and network formation in the rubber vulcanizate. High surface area as such may not be the basic cause of high conductivity, but is probably a phenomenon associated with other changes in the black which are responsible for the observed effects on resistivity.

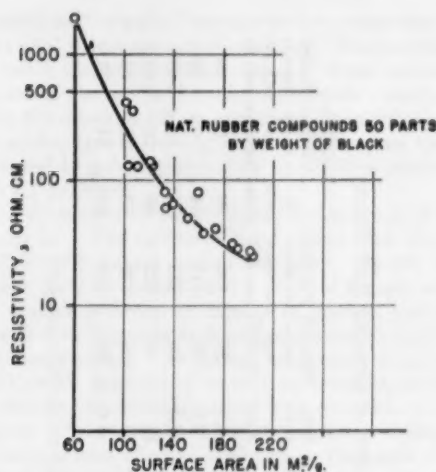


Fig. 8.—Relation of surface area of oil furnace blacks to resistivity.

Performance of High Surface-Area HAF Samples Prepared in the Laboratory.—This opinion regarding surface area and electrical conductivity is based on results obtained with a series of oxidized HAF blacks prepared in an externally heated laboratory furnace. The procedure is similar to the one mentioned under the heading, "characteristics of blacks with increasing surface area," but on a larger scale. Therefore the semi-technical oxidation is a slower process than the analytical procedure which was followed to find the points of Figure 2. The furnace consisted of a rotating horizontal tube, which was maintained at a temperature of 400° to 500° C. A slow stream of air was maintained through the oven, which was filled with about 400 grams of unpelletized black, allowing enough free space to assure uniform exposure to the air during treatment. A range of surface areas was produced by varying the time of treatment in the furnace. Oxidation at temperatures of 400° to 500° C produces blacks which retain appreciable quantities of chemisorbed surface oxygen. The chemisorbed

TABLE II
PROPERTIES OF LABORATORY-PREPARED OXIDIZED,
AND DEVOLATILIZED HAF SAMPLES^a

Air used for oxidation (cu. m./kg. at 30° C)	Nitrogen adsorption surface area (sq. m./g.)	Electron microscope diameter average (m μ) ^b	Nigrom- eter scale	Tinting strength, SRF at 100
—	71	29	90	150
0.37	149	—	90	160
0.62	245	—	89	163
0.91	273	—	88	162
1.40	319	30	89	160
3.00	504	—	87	163

^a Unpelletized HAF heated in air stream at 565° to 580° C, followed by devolatilization at 935° C. (Volatile on all 935° C samples was 1.3 to 2.1%.)

^b End²
End²

TABLE III
PROPERTIES OF NATURAL RUBBER COMPOUNDS CONTAINING 40 PARTS OF OXIDIZED HAF BLACK^a

Air used for oxidation (cu. m./kg.)	Oxygen used per carbon atom		Nitrogen in surface area ^b (sq. m./g.)	Increase in N ₂ surface area		300% Modulus (lb./sq. inch)	Tensile strength (lb./sq. inch)	T-50 (° C)	Resis- tivity (ohm-cm. × 10 ⁹)	Rebound resili- ence (% R.E.)	Relative lab. abra- sion resist- ance (%)	% Bound rubber	Estd. % increase in no. of particles (ML 10/ 250° F)
	Mole O ₂	Atom O		(sq. m./g.)	(sq. m./ % loss ^b)								
—	—	—	71	—	—	1730	4480	-11.1	1.1	77	100	30	0
0.37	0.033	0.07	149	78	24	1860	4500	-6.6	2.2	75	118	34	6
0.62	0.056	0.11	245	174	31	1990	4610	-4.7	6.5	76	113	38	14
0.91	0.082	0.16	273	292	25	2000	4600	-2.1	14	76	127	46	16
1.40	0.125	0.25	319	248	20	2000	4800	+1.6	25	76	138	55	20
3.0	0.27	0.54	504	441	16	2180	4290	+3.8	5.6	73	162	64	34

^a 2.7 parts of sulfur, 0.7 part of Santocure, 30 minute cure at 138° C. Shore hardness 65 to 66.

^b Loss based on oxidation to CO₂. 15 A. line in Figure 2 indicates about 15 sq. m./g. increase in surface area per % loss of weight.

oxygen was liberated as "volatile," mainly carbon monoxide, by an additional heat treatment at 955° C in a stream of nitrogen. During this heat treatment, volatile weight losses increased almost linearly with increased surface area. The heat treatment of the oxidized blacks to remove volatile was necessary in order to eliminate the effect of pH on cure rate, since volatile in the quantities found produces acidic, slower curing blacks. Therefore these samples were carefully heat-treated to give a slurry with an alkaline reaction and a volatile content of 1.3 to 2.1 per cent.

The analytical properties of these laboratory samples of high surface area are shown in Table II. The second column shows that the surface area was increased from 71 to 504 square meters per gram. In the third column, the electron microscope particle counts on the original sample and the 319-square meters-per-gram sample indicate no change in particle size during oxidation. The next columns, listing Nigrometer scale and tinting strength value show little change in color characteristics. As jetness is closely related to particle size, it may be assumed that no appreciable change occurred in particle size.

Table III shows the properties obtained with these blacks in natural rubber at a 40-part loading. This is the group of experiments which upset the picture of porosity and surface area effects developed as the basis of the performance of directly produced furnace blacks of high surface area. The only confirmation of the performance of direct furnace-produced blacks with these laboratory-oxidized samples was obtained in respect to relationship for surface area with rate of cure. The low temperature retraction values (*T*-50) show a progressive decrease of state of cure and the rate of tensile strength development (not shown in table) also indicated a retardation of curing rate with increasing surface area.

Resistivity and rebound, however, do not follow the previously observed trends. Here the resistivity actually increases with increasing area, in marked contrast to the results obtained with the experimental furnace blacks. Rebound remains unchanged except for the extreme sample of 504 square meters per gram. These trends indicate a lack of chain and network formation in the vulcanizates. For this reason, surface area alone cannot be the basic cause of the increased conductivity previously observed. Increased abrasion resistance and a trend toward higher tensile and modulus values indicate greater reinforcement with increased particle porosity. It is felt that the increased effective volume loading resulting from particle porosity, estimated in the last column, cannot account for the higher level of reinforcement. It is possible that these effects are due to a larger number of attachments of rubber molecules to the highly extended particle surfaces. Evidence supporting this possibility is presented in the percentage of bound rubber after 6 days' aging of the vulcanized stocks measured by a 24-hour benzene extraction at room temperature. Bound rubber increases regularly with surface area, indicating enhanced bonding of the rubber phase. The increase of Mooney viscosity shown in the last column is probably associated with the same phenomenon.

It is interesting to compare weight loss and increase of surface area with these same technical scale-treated blacks. The only available entity is the amount of oxygen used and, if all of this is assumed to react to carbon dioxide, a much more efficient increase in surface area would be found than that shown in Figure 2 for 15 A. pores. Actually, the surface area increase per per cent weight loss was about double that of 15 A. pores. If all oxygen reacted to give carbon monoxide, the data would be concordant with 15 A. pores. Thermodynamics indicate an equilibrium which lies completely on the carbon dioxide

side. This may mean a pore diameter of roughly 7.5 Å, which is about the distance between the graphitic planes in the crystallites⁸.

Columns 2 and 3 of Table III show the relative weight losses of the black in case of oxidation to carbon dioxide and monoxide, respectively.

SUMMARY

Porous blacks of high surface area can be produced without changing particle size either directly, in the normal furnace black process, or indirectly, in the laboratory by the air oxidation of a normal commercial and essentially nonporous HAF black raw material. Blacks of high surface area produced by the direct process are characterized by a retardation of rate of vulcanization, lower rebound resilience, and high electrical conductivity. Laboratory-prepared products of high area show cure retardation, but their electrically conductive and resilience properties show relatively little dependence on the degree of porosity and surface area. Bound rubber measurements, modulus, tensile strength, and abrasion properties of the laboratory-oxidized samples indicate an increase of reinforcement with increasing surface area.

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STRUCTURE AND DIELECTRIC PROPERTIES OF RUBBER MIXTURES CONTAINING CARBON BLACK *

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One of the fundamental steps in solving the problem of the reinforcement of rubber is that of explaining the nature of the reaction between rubber and fillers. The measurement of heat effects during swelling¹, in addition to presenting experimental difficulties, does not provide a direct evaluation of the intensity of the rubber-filler bond in rubbers used in industry. In order to measure this bond, the present authors studied the frequency and temperature relations of the dielectric constant ϵ' and the tangent of the angle of dielectric losses, $\tan \delta$, of unvulcanized natural rubber and sodium-butadiene rubber, rubber-carbon black mixtures, and vulcanized rubber containing different loadings of channel and furnace blacks.

The measurements were made in the frequency range of 50 to 2.5×10^7 cycles per second at 20° C and also in the frequency range of 10^3 to 4×10^4 cycles per second at temperatures from -75° to 152° C. As the experiments show (see Figure 1), the coefficient of dielectric loss, $\epsilon'' = \epsilon' \cdot \tan \delta$, of a raw rubber has no maximum within the frequency range and temperature range studied. At the same time, the rubber-carbon black mixtures are characterized by a maximum ϵ'' at frequencies of $(2-2.5) \times 10^3$ cycles per second, which depends to a slight extent on the temperature. Vulcanizates containing no carbon black have a maximum ϵ'' at $(2-3.5) \times 10^6$ cycles per second at 20° C, which is displaced to the temperature range -24° to -27° when the frequency is decreased to 10^3 cycles per second. Both maxima are observed on the ϵ'' curves with loaded vulcanizates, the first caused by the heterogeneity of the rubber-carbon black mixture, and the second due to the formation of sulfur dipoles during vulcanization. Consequently, the ϵ' curves have two regions of change.

The ϵ' and ϵ'' curves of two-component mixtures can be expressed by the equations for a heterogeneous dielectric² if there is subtracted from the experimental value of ϵ'' a certain value ϵ''_{str} , which is constant for any particular mixture, and a value ϵ''_{SBR} , calculated from the equation:

$$\epsilon''_{SBR} = \frac{1.8 \times 10^{13} \sigma}{f}$$

where σ is the direct-current conductivity in mho and f is the frequency in cycles per second.

Thus there are three kinds of dielectric losses when rubber contains carbon black: (1) losses from the non-uniform dielectric; (2) losses by conductivity, and (3) losses caused by structure formation. The physical character of the

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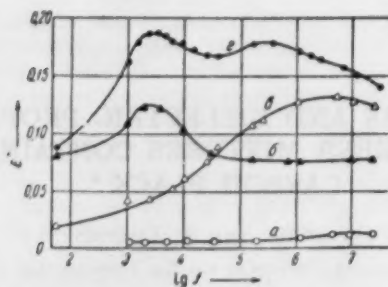


FIG. 1.—Coefficient of dielectric loss ϵ'' as a function of the frequency f at 20° C. Curve a. Raw sodium-butadiene rubber. Curve b. Unvulcanized sodium-butadiene rubber-channel black mixture (10 volumes of carbon black). Curve c. Unloaded vulcanizate of sodium-butadiene rubber. Curve d. Sodium-butadiene rubber-carbon black vulcanizate (10 volumes of channel black). Following the right-hand side of the diagram, Curve a is the lowest, Curve b is next above a, Curve c is next to the topmost curve, and Curve d is the topmost curve.

latter has not yet been determined. It can be assumed that the separate groups of atoms in the rubber molecules are polarized in a field of carbon-black particles, and when the rubber molecules in the amorphous state are loosely packed³, they acquire the property of oscillating in an electric field. The value of ϵ''_{stv} depends on both the content and type of carbon black and on the type of rubber.

An example of the division of the experimental curve of ϵ'' into components in the case of loaded vulcanizates is shown in Figure 2. The ϵ''_{dip} curves of loaded vulcanizates, as well as the experimental relations of ϵ'' for carbon-free vulcanizates, satisfy the equation:

$$\epsilon''_{dip} = \epsilon''_{max} \cdot \text{sech}(\alpha, \chi)$$

where ϵ''_{max} is the value of ϵ'' at maximum (at f_M); $\chi = \ln(f_M/f)$; f is the frequency at which ϵ''_{dip} is located, and α is the parameter of distribution of relaxation times⁴. Here f_M is the exponential function $1/T$, where T is the

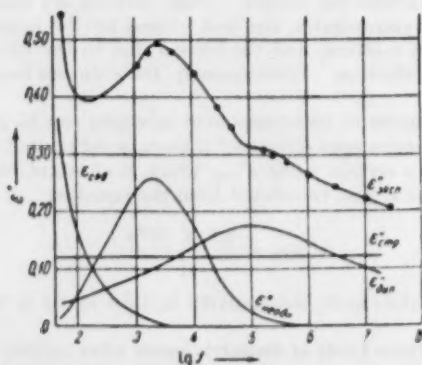


FIG. 2.—Frequency curves at 20° C. Experimental coefficient of loss ϵ''_{exp} , and coefficient of loss: conductivity ϵ''_{stv} in non-uniform dielectric structural ϵ''_{stv} , and dipolar ϵ''_{dip} (vulcanized sodium-butadiene rubber containing 15 volumes of carbon black). At the left-hand ordinate of the diagram, the bottom curve is $\epsilon''_{non-unif}$; the next curve is ϵ''_{stv} ; the next curve (horizontal line) is ϵ''_{stv} ; the curve above this is ϵ''_{dip} ; the top curve is ϵ''_{exp} .

absolute temperature, and the parameter α increases with increase of temperature to a maximum value α_{\max} , which is reached at 100–120° C, and is independent of the loading, like the dipolar moment of vulcanization, calculated for a monomeric unit of rubber according to the relation:

$$\bar{\mu} = 0.0127 \sqrt{\frac{M}{\rho} \cdot \frac{4 \cdot \epsilon''_{\max}}{9\alpha} \cdot GT \cdot 10^{-18}}$$

where M is the molecular weight of the monomer, and ρ and G are the density and volumetric content, respectively, of the rubber phase in the vulcanizate. The analogous change of $\bar{\mu}$ and α_{\max} indicates the absence of any chemical reaction between the rubber and filler. In fact, the series of relaxation times is determined by both the nature of the intermolecular reaction in the mixture and the molecular structure of the polymer itself. At high temperatures, the energy of heat movement is so great that the intermolecular reaction can be disregarded. The α_{\max} value will then depend only on the type of polymer ($\alpha_{\max} = 0.435$ for natural rubber and 0.283 for sodium-butadiene rubber. If loading does not cause the formation of new chemical bonds in the polymer, the presence of a filler will have no influence on the value of α_{\max} , as was observed experimentally.

Proceeding from the exponential relation of f_M to $1/T$, the energy of activation of dipolar orientation U can be calculated according to the equation:

$$\frac{1}{2 \cdot \pi \cdot f_M} = \tau_0 = A \cdot e^{U/(RT)}$$

where T_0 is the most probable relaxation time. According to Debye,

$$\tau_0 = \frac{4 \cdot \pi \cdot \eta \cdot a^2}{k \cdot T}$$

In the case of orientation of the sulfur dipoles in vulcanized rubber, η , represents the "microscopic" viscosity, corresponding to the displacement of the segments of the molecular chains by the quantity a (dielectric segments). In order to find the relation of viscosity to loading, the deformation of mixtures containing several ingredients was studied with a Hepler consistometer and a Kornfeld apparatus. The results show that the relation of the viscosity of a loaded mixture to the viscosity of an unloaded mixture does not depend in first approximation on the conditions (stresses, frequency, temperature) or on the testing equipment (consistometer or Kornfeld apparatus). This fact makes it possible to calculate, by Debye's formula, the relative change of a due to swelling, using relative viscosity values.

The relations of U , a , and α to the loading are presented in Table 1. The values of the form factor ϕ , which expresses the relation of the amount of carbon structure in the mixture to the values determined according to the following formula, are also given:

$$(\epsilon_e)_{\text{non-un.}} = \epsilon'_1(1 + 3\phi \cdot p)$$

where $(\epsilon_e)_{\text{non-un.}}$ is the dielectric permeability ϵ' in the frequency range where the change of ϵ' is practically complete for a non-uniform dielectric; ϵ'_1 is the dielectric permeability of the rubber phase of the vulcanizate; and p is the volume content of the carbon black phase.

As is evident from Table 1, there is a direct relation between the changes of U , a and α and the change of ϕ . If $\phi \approx 1$, U increases with loading, and a and

TABLE I

Carbon black content in cc. per 100 grams of rubber	ϕ	U kcal. per mol	α	a
Vulcanized Natural Rubber				
(a) Channel black				
0.0	—	23.8	0.425	a_K
5.0	1.07	28.4	0.415	1.03 a_K
10.0	2.51	27.5	0.421	1.49 a_K
(b) Furnace black				
10.0	1.0	26.7	0.424	1.01 a_T
20.0	1.11	26.6	0.426	1.01 a_T
Vulcanized Sodium-Butadiene Rubber				
(a) Channel black				
0.0	—	26.6	0.264	a_e
5.0	1.00	31.8	0.279	1.1 a_e
7.5	1.20	31.7	0.23	1.286 a_e
10.0	1.715	31.5	0.246	1.875 a_e
15.0	3.21	25.0	0.310	2.32 a_e
20.0	5.02	17.0	0.330	2.23 a_e
(b) Furnace black				
10.0	1.0	31.4	0.24	1.015 a_e
20.0	1.07	34.5	0.211	1.01 a_e
30.0	1.0	35.10	0.206	a_e

α change little. If $\phi > 1$, U is reduced by loading, while a and α increase noticeably. Thus, the change of the characteristics of dipolar orientation is determined by the presence or absence of carbon-black chain structures in the mixture.

The direct connection between the capacity of any type of black to form carbon black structures and the reinforcing properties of the carbon black has been established by other investigations⁶. Carbon black structures are formed by the contact between particles of carbon black, i.e., carbon-carbon bonds. We established that the relations of the logarithm of the electric conductivity of a mixture to $1/T$ remains linear up to high temperatures (150° C). This relation indicates the strength of the carbon-carbon bond. At the same time, the influence of carbon black on the orientation of dipoles in rubber, by the rubber-carbon bonds, ceases to be appreciable at 100–120° C, in which range the maximum value of α_{\max} is established. Accordingly, it can be concluded that the formation of carbon structures in a mixture in which the reaction between the carbon black particles exceeds the reaction between the rubber and filler, is of great importance in determining the properties of a loaded vulcanizate, particularly its mechanical properties, since there is a certain analogy between the behavior of rubber in an electric and a mechanical field⁷.

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PROMOTERS FOR THE REACTION OF RUBBER WITH CARBON BLACK *

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INTRODUCTION: HEAT TREATMENT OF RUBBER AND CARBON BLACK IN ABSENCE OF PROMOTERS

It was discovered by Gerke, Ganzhorn, Howland, and Smallwood¹ and by Bradley² that heat-treating an unvulcanized mixture of Hevea rubber and carbon black, with simultaneous or subsequent mastication, changed the physical properties of the resulting vulcanizate. The heat-treated stock has increased electrical resistivity, reduced torsional hysteresis and durometer hardness, higher modulus at large deformations, and increased abrasion resistance. Heating times of 10-60 minutes in the range 300-375° F were required to obtain an extensive treatment. Typical results obtained with a mixture of Hevea rubber and channel (MPC) black are shown in Table I. Heat treatment

TABLE I
EFFECT OF HEAT TREATMENT (350° F) OF MIXTURE OF HEVEA
RUBBER AND 50 PARTS OF CHANNEL (MPC) BLACK

Time (minutes)	Log R*	Torsional hysteresis (280° F)	Shore durometer	200% stress
0	6.8	0.181	65	1500
3	8.2	0.093	62	1700
6	8.8	0.088	62	1725
12	11.4	0.062	60	1800
30	> 13.0	0.052	58	1875

* Resistivity.

of Hevea rubber containing 75 parts of black was carried out at 350° F in a laboratory Banbury. Prior to vulcanization, additional Hevea rubber was added to give a concentration of 50 parts of black.

A mixture of Butyl rubber (GR-I) and carbon black³ also responds to heat treatment, giving similar changes in physical properties. Butadiene-styrene copolymers (GR-S) also respond to heat treatment.⁴ Butyl rubber, because of its low unsaturation, requires higher temperatures or longer times than Hevea rubber or GR-S. The relative reactivities can be demonstrated by a comparison of the electrical resistivities of stocks which received different times of heating at 375° F prior to vulcanization. Table II shows the logarithm of resistivities (in ohm-centimeters) for Hevea rubber, GR-S (containing 23.5 per cent styrene, polymerized at 41° F), and two types of Butyl rubber, which differ in the amount of unsaturation, GR-I-25 having higher unsaturation than GR-I-15. All stocks contained 50 parts of a medium-processing channel

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(MPC) black. The heat treatment was carried out in a laboratory Banbury mixer.

Hevea rubber and GR-S, which are highly unsaturated, respond to the heat treatment many times more rapidly than Butyl rubber. The presence of the amine antioxidant BLE appears to retard the process slightly in Hevea rubber. GR-I-25 is somewhat more reactive than GR-I-15, because of its higher unsaturation. With Butyl rubber, as well as with Hevea, increases of log resistiv-

TABLE II
EFFECT OF HEAT TREATMENT (375° F) ON RESISTIVITY (R) OF MIXTURES OF RUBBERS AND 50 PARTS OF CHANNEL (MPC) BLACK

Time (minutes)	Log R				
	Hevea	Hevea†	GR-S	GR-I-15	GR-I-25
0*	6.9	6.9	7.4	5.6	5.6
4	10.4	9.6	—	—	—
8	>13.0	11.6	12.8	—	—
15	>13.0	>13.0	>13.0	—	—
30	—	—	—	6.9	7.8
50	—	—	—	8.6	11.0
120	—	—	—	>13.0	>13.0

* At zero time log R of conventionally prepared masterbatch, prior to heat treatment, is given.

† 1.5 parts of commercial antioxidant, BLE, was added prior to heat treatment.

ity are paralleled by decreases of torsional hysteresis. Mixtures of carbon black and Vistanex, which contain no unsaturation, do not have their resistivity changed by heat treatment⁶.

EFFECT OF CHEMICAL PROMOTERS ON THE HEAT TREATMENT OF HEVEA OF BUTYL RUBBER AND CARBON BLACK

Several chemicals have been reported to decrease the time or temperature required to give an extensive treatment. Howland⁶ used small amounts of

TABLE III
COMPARISON OF PROMOTERS IN MIXTURE OF HEVEA RUBBER AND 50 PARTS OF CHANNEL (MPC) BLACK*

Promoter†	Time (minutes)	Log R	Torsional hysteresis 280° F
None	20	8.4	0.115
None	120	>13.0	0.068
<i>p</i> -Nitrosodiphenylamine	20	>13.0	0.057
<i>p</i> -Quinone dioxime	20	>13.0	0.050
<i>p</i> -Nitrosodimethylaniline	20	>13.0	0.060
Tetrachloro- <i>p</i> -quinone	20	>13.0	0.071
Tetrachloro- <i>p</i> -quinone	120	>13.0	0.061

* Heat treatment was static, in open steam at 300° F.

† 0.005 moles per 100 parts of rubber.

quinones, such as *p*-quinone dioxime, and aromatic nitroso compounds, such as *p*-nitrosodiphenylamine and *p*-nitrosodimethylaniline, in Hevea rubber containing carbon black. Some of the promoters described in Howland's patents were used by Gessler and Ford⁷ in mixtures of Butyl rubber and carbon black. Thus, *p*-dinitrosobenzene (commercially known as Polyac) and *p*-quinone dioxime, as well as sulfur and certain sulfur-bearing compounds, were effective, Howland also used certain diprimary amines, such as *p,p'*-diaminodiphenyl-

methane (commercially known as Tonox) and benzidine⁸. Gerke used hydrazine⁹ and urea¹⁰, while Barton used tetrachloro-*p*-quinone¹¹.

Since short reaction times are desirable if the process is to be used commercially, a study has been made of the relative effectiveness of a large number of chemical promoters. This included some previously reported ones, as well as many new ones for Hevea rubber, GR-S, or Butyl rubber.

The effect of several previously reported promoters in a mixture of Hevea rubber and channel (MPC) black is shown in Table III. In all experiments, a black masterbatch, containing 50 parts of black and five parts of stearic acid, was prepared in a conventional manner. The promoters were mixed into the black masterbatch on a mill. Heat treatment was carried out statically in open steam at 300° F. The stocks were then remilled and compounded in a

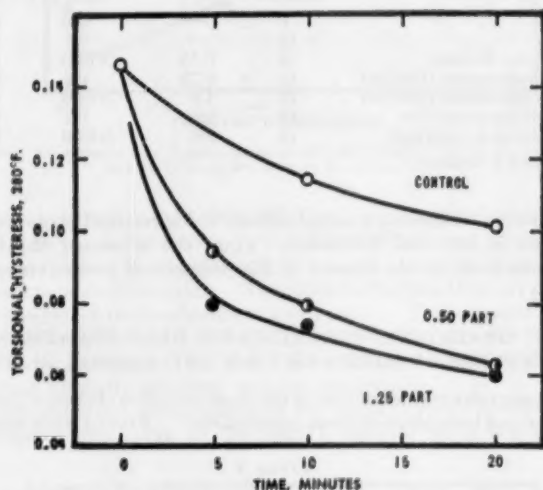


FIG. 1.—Effect of *p*-nitrosodimethylaniline on heat treatment of Hevea rubber and 50 parts MPC black, in Banbury at 300° F.

normal manner. Resistivity and torsional hysteresis were measured as previously described¹².

The most reactive compounds are *p*-quinone dioxime and the aromatic nitroso compounds, *p*-nitrosodiphenylamine, and *p*-nitrosodimethylaniline. Tetrachloro-*p*-quinone is slightly less effective, but in 20 minutes gives a result about equivalent to 120 minutes in absence of a promoter.

The effect of concentration of one promoter, *p*-nitrosodimethylaniline, and time of treatment are shown graphically in Figure 1. The heat treatment was carried out at 300° F in a laboratory Banbury mixer for various times up to 20 minutes. Acceleration was adjusted to compensate for the activating effect of the promoter. As expected, the higher concentration, 1.25 parts per 100 parts of rubber, gives a faster reduction of torsional hysteresis, but after 20 minutes treatment shows little advantage over 0.50 part.

Several promoters were compared in Butyl rubber (GR-I-15) containing 50 parts of channel (MPC) black and three parts of stearic acid. The promoters

were mixed into the masterbatch on a mill, followed by heat treatment in the Banbury for 15 minutes at 375° F. The higher temperature was used because of the relatively low reactivity of Butyl rubber. The results are shown in Table IV.

Both *p*-quinone dioxime and *p*-dinitrosobenzene are very effective. Tetrachloro-*p*-quinone is less reactive in GR-I-15. Although it increased log resistivity to 9.2, there was only a small effect on torsional hysteresis. In

TABLE IV
EFFECT OF PROMOTERS ON HEAT TREATMENT (375° F) OF MIXTURE
OF GR-I-15 AND 50 PARTS OF CHANNEL (MPC) BLACK*

Promoter	Time (minutes)	Parts	Log R	Torsional hysteresis 280° F
None	0	—	5.6	0.300
None	15	—	6.7	0.165
<i>p</i> -Quinone dioxime	15	0.75	>13.0	0.065
Dinitrosobenzene (Polyac)	15	0.75	9.9	0.094
Dinitrosobenzene (Polyac)	15	1.5	>13.0	0.073
Tetrachloro- <i>p</i> -quinone	15	2.0	9.2	0.150
Tetrachloro- <i>p</i> -quinone†	15	2.0	>13.0	0.075

* Heat treatment in Banbury.

† In GR-I-25.

GR-I-25, however, it showed a larger change of log resistivity, and a characteristic reduction in torsional hysteresis. Thus, the increased unsaturation increases the reactivity of the system in the presence of promoters as well as in their absence.

EFFECT OF ORGANIC PEROXIDES ON HEAT TREATMENT OF MIXTURES OF HEVEA OR GR-S AND CARBON BLACK

Organic peroxides represent one of the most effective classes of promoters for Hevea rubber and butadiene-styrene copolymers¹². From a wide variety tested,

TABLE V
EFFECT OF *t*-BUTYL PERBENZOATE ON MIXTURE OF HEVEA RUBBER AND
50 PARTS OF CHANNEL (MPC) BLACK*

Parts peroxide	ML-4 212° F	Log R	Torsional hysteresis 280° F	Stress (300%)	Scott tensile strength
0.00	46	6.8	0.196	1525	3840
0.30	41	7.5	0.121	1650	3850
0.60	35	9.7	0.094	1800	3740
1.00	31	>13.0	0.055	1900	3530
1.60	29	>13.0	0.048	2000	2970

* Heat treatment, 5 min. at 300° F on small mill, including control.

t-butyl perbenzoate and cumene hydroperoxide (α,α -dimethylbenzyl hydroperoxide) are among the most effective.

The effect of *t*-butyl perbenzoate on a mixture of Hevea rubber and 50 parts of channel (MPC) black is shown in Table V. The peroxide was mixed into the black masterbatch at a temperature below 225° F. The mixtures were then heated on a mill for five minutes, with a stock temperature of about 300° F, a time and temperature sufficient to decompose nearly all the peroxide. The control received the same heat treatment.

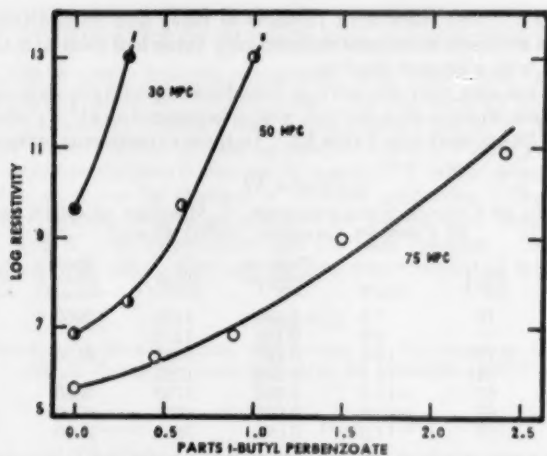


FIG. 2.—Effect of *t*-butyl perbenzoate on electrical resistivity of Hevea rubber and MPC black, five minutes on mill at 300° F.

t-Butyl perbenzoate is extremely effective in increasing electrical resistivity and reducing torsional hysteresis. Modulus (300 per cent stress) is progressively increased, while tensile strength is lowered less than 10 per cent by the use of up to one part of peroxide. The stock properties thus are characteristic of the heat treatment in the absence of a promoter. The peroxide progressively reduces the Mooney viscosity of the compounded stock prior to vulcanization. However, the values recorded in Table V were obtained on a laboratory mill, and are lower than normally obtained on large equipment.

The effect of *t*-butyl perbenzoate on log resistivity and torsional hysteresis of Hevea rubber containing 30, 50, and 75 parts of MPC black is shown in

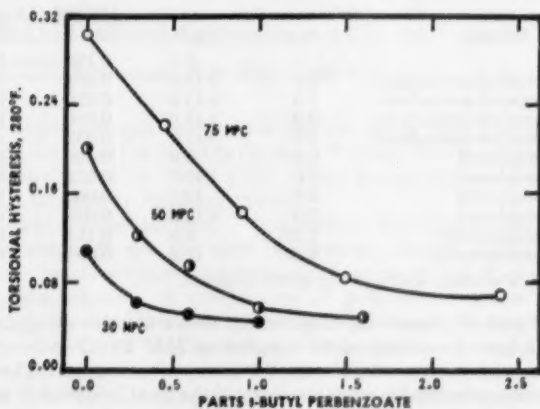


FIG. 3.—Effect of *t*-butyl perbenzoate on torsional hysteresis of Hevea rubber and MPC black, five minutes on mill at 300° F.

Figures 2 and 3. The stock with 75 parts of black and no additional Hevea rubber has its torsional hysteresis reduced to a value less than half that normally obtained with a 50-part loading.

Peroxides are also very effective in butadiene-styrene copolymers, such as GR-S containing 23.5 per cent styrene, and polymerized at 41° F. Some representative results are shown in Table VI. In these experiments, cumene hydro-

TABLE VI
EFFECT OF CUMENE HYDROPEROXIDE ON MIXTURE OF GR-S AND
52 PARTS OF CHANNEL (MPC) BLACK*

Parts peroxide†	ML-4 212° F	Log R	Torsional hysteresis 280° F	Stress (300%)	Scott tensile strength	Abrasion resistance
None†	75	7.9	0.180	1100	2980	100
None	—	9.0	0.145	1275	—	—
0.6	77	10.6	0.107	1525	3130	115
1.0	81	11.4	0.102	1725	—	120
1.5	87	>13.0	0.092	1750	3050	125
2.0	92	>13.0	0.083	1925	2790	125
None‡	77	11.6	0.099	1625	2900	120

* X-680 GR-S, a latex masterbatch, was used. The stocks contained six parts of hydrocarbon softener. Heat treatment was in Banbury with temperature rise from 275 to 325° F in eight minutes.

† Did not receive heat treatment.

‡ Commercial sample, 72% peroxide.

§ Heat treated for 10 minutes at about 365° F.

peroxide was mixed into a black masterbatch, which was heat-treated in a laboratory Banbury mixer with a temperature rise from 275° to 325° F in eight minutes. The stocks were all compounded with equivalent sulfur and accelerator level.

Cumene hydroperoxide thus increases electrical resistivity, reduces torsional hysteresis, increases stress at 300 per cent elongation, and increases abrasion

TABLE VII
EFFECT OF ACTIVE HALOGEN COMPOUNDS ON MIXTURES OF HEVEA
RUBBER AND 50 PARTS OF CHANNEL (MPC) BLACK*

Promoter	Parts	Log R	Torsional hysteresis 280° F	Stress (300%)
None	—	8.1	0.120	1500
Hexachlorocyclopentadiene	0.5	>13.0	0.061	1700
Hexachlorocyclopentadiene	1.0	>13.0	0.056	1775
Hexachlorocyclopentadiene	2.0	>13.0	0.050	1825
Hexachlorocyclopentadiene	2.7	>13.0	0.052	1950
Hexachlorophenol	0.5	9.0	0.098	1500
Hexachlorophenol	1.0	10.7	0.076	1625
Hexachlorophenol	2.0	12.6	0.063	1750
Hexachlorophenol	3.0	>13.0	0.048	1950
N-Chlorosuccinimide	1.20	9.8	0.101	1500
N-Bromosuccinimide	1.64	10.2	0.084	1500

* Heat treatment of all stocks was for 10 min. at 300° F on mill.

resistance; 1.0 part of cumene hydroperoxide under these conditions is about equivalent to a heat treatment of 10 minutes at 365° F. Tensile strength is not reduced, except for the stock with 2.0 parts of peroxide. The peroxide causes some increase in the Mooney viscosity of the final compound, in contrast with the effect in Hevea rubber. The minimum torsional hysteresis is higher than that obtained with Hevea rubber.

EFFECT OF ACTIVE HALOGEN COMPOUNDS ON HEAT TREATMENT OF RUBBER AND CARBON BLACK

A number of active halogen compounds have been found to promote the heat treatment of rubber and carbon black. Among these are hexachlorocyclopentadiene¹⁴, hexachlorophenol¹⁵, and *N*-halogenated imides¹⁴. Typical results obtained in Hevea rubber containing channel black are shown in Table VII. Hexachlorocyclopentadiene is very reactive at 300° F, while hexachlorophenol is less reactive, as shown by changes in physical properties. Thus, 0.5 part of hexachlorocyclopentadiene is as effective as 2.0 parts of hexachlorophenol. *N*-Chloro- and *N*-bromosuccinimide are the least reactive. These chemicals are also effective in GR-S, although no data are presented at this time.

TABLE VIII
EFFECT OF ACTIVE HALOGEN COMPOUNDS ON MIXTURES OF GR-I-15
AND 50 PARTS OF CARBON BLACK, 20 MINUTES AT 375° F.

Promoter	Parts	ML-4 212° F	Log R	Torsional hysteresis 280° F
<i>Channel (MPC) Black</i>				
None*	—	60	5.6	0.300
None†	—	64	6.9	0.170
Hexachlorocyclopentadiene	1.5	58	>13.0	0.055
Hexachlorophenol	1.5	51	>13.0	0.084
1,3-Dichloro-5,6-dimethylhydantoin	1.5	65	>13.0	0.062
<i>N</i> -Chlorosuccinimide	1.5	62	>13.0	0.077
<i>N</i> -Bromosuccinimide	1.5	57	>13.0	0.061
Dinitrosobenzene (Polyac)	1.5	66	>13.0	0.073
<i>Furnace (HAF) Black</i>				
None†	—	79	2.9	0.195
Hexachlorocyclopentadiene	2.0	—	>13.0	0.092
1,3-Dichloro-5,5-dimethylhydantoin	2.0	74	7.9	0.072
<i>Furnace (ISAF) Black</i>				
None†	—	86	2.7	0.255
Hexachlorocyclopentadiene	2.0	76	8.6	0.084
1,3-Dichloro-5,5-dimethylhydantoin	2.0	82	8.0	0.099

* No heat treatment.

† Control received heat treatment of 20 minutes at 375° F.

These active halogen compounds are also quite effective in GR-I-15 containing either channel or furnace blacks. Typical results obtained with different blacks are shown in Table VIII. Heat treatment was for 20 minutes at 375° F in a laboratory Banbury mixer.

Hexachlorocyclopentadiene, 1,3-dichloro-5,5-dimethylhydantoin, and *N*-bromosuccinimide are the most reactive in channel (MPC) black stocks. Slightly less reactive (based on torsional hysteresis) are *N*-chlorosuccinimide and hexachlorophenol. A comparison of *p*-dinitrosobenzene (Polyac) with hexachlorocyclopentadiene and 1,3-dichloro-5,5-dimethylhydantoin at different temperatures is shown in Figure 4. (Comparison is on equal weight basis.) The active halogen compounds are approximately equivalent in the temperature range 325–375° F, and appear to be slightly superior to *p*-dinitrosobenzene, although differences are small.

Both hexachlorocyclopentadiene and 1,3-dichloro-5,5-dimethylhydantoin

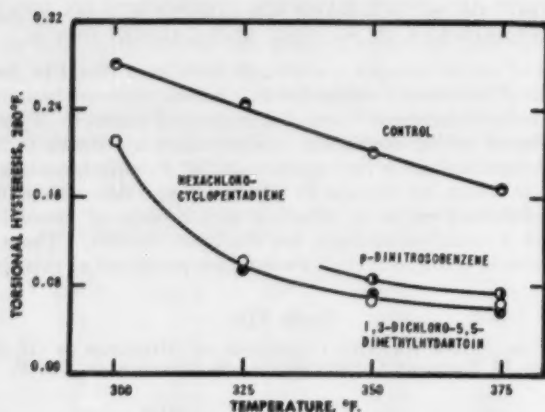


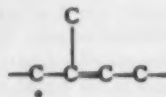
FIG. 4.—Effect of promoters (1.5 parts) on torsional hysteresis of GR-I-15 and 50 parts MPC black, 20 minutes in Banbury at various temperatures.

are effective promoters for GR-I-15 containing high abrasion furnace (HAF) black and superabrasion furnace types (ISAF), also shown in Table VIII.

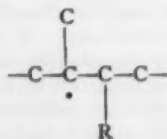
DISCUSSION: MECHANISM OF ACTION OF PROMOTERS

It has been suggested that the heat treatment of rubber and carbon black causes the formation of permanent chemical bonds between rubber chains and carbon black particles¹⁶. Hevea rubber shows an over-all activation energy of about 18,000 calories, based on the rate of change of log resistivity⁶. Butyl rubber shows an over-all activation energy of 16,000 calories, based on the increase of 300 per cent stress¹⁷. The rate depends on the degree of unsaturation of the rubber, and the amount of oxygen on the black¹⁸. The bound rubber content increases as the extent of the treatment increases. Although electron micrographs show no definite changes in dispersion of the carbon black⁶, it has been suggested that the chemical bonding of rubber to carbon black particles, followed by mastication, improves the dispersion of carbon black sufficiently to give the marked changes in electrical resistivity and other properties¹⁹.

The high efficiency of peroxides in promoting the process, and the apparent retardation by antioxidants (Table II), strongly suggests that a free radical reaction is involved. Presumably free radicals, $R\cdot$, formed by decomposition of peroxides can attack α -methylene groups or double bonds in the rubber chains, forming allylic radicals A, as well as some alkyl radicals B, in a Hevea rubber chain²⁰.

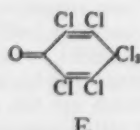
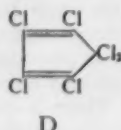


A



B

The active halogen compounds, hexachlorophenol and hexachlorocyclopentadiene, conceivably can form free radicals by loss of a chlorine atom from a carbon atom adjacent to two double bonds, as in D and E. This chlorine atom should be quite active.



However, it has recently been shown that hexachlorocyclopentadiene adds to olefins (in the absence of carbon black) in a Diels-Alder reaction²¹. This reaction apparently is not affected by free radicals or phenolic inhibitors. This opens the possibility that there may also be an ionic mechanism in the reaction of rubber and carbon black.

An alternative mechanism is available for the bifunctional vulcanizing agents²², such as *p*-dinitrosobenzene and tetrachloro-*p*-quinone. They may have one group bonded to a rubber chain and the other to a carbon black particle. When used in vulcanization, at least part of these agents are chemically bonded to the rubber chain²³. There is also some reduction to tetrachloro-hydroquinone and *p*-quinone dioxime²⁴, suggesting that allylic rubber radicals are formed by loss of α -hydrogen atoms. *p*-Quinone dioxime may function similarly to *p*-dinitrosobenzene, since it is readily oxidized to *p*-dinitrosobenzene. Channel black renders it active, presumably because of oxygen on the surface²⁵.

Sulfur may also form a cross-link between rubber and carbon black²⁶. Sulfur is believed to cause the formation of allylic radicals in rubber²⁷, which might react with carbon black. However, there are insufficient data to decide whether these vulcanizing agents actually form cross-links between rubber and carbon black, or merely initiate rubber free radicals, which then add to carbon black.

SUMMARY

Heating unvulcanized mixtures of rubber and carbon black gives increased electrical resistivity, reduced hysteresis and hardness, higher modulus, and increased abrasion resistance to the vulcanizate. This is believed to result from improved dispersion of carbon black, accompanying a chemical reaction between rubber and carbon black. Butyl rubber, with low unsaturation, reacts more slowly than Hevea rubber or butadiene-styrene copolymers (GR-S). Chemical promoters decrease the time and temperature required for the reaction. Certain quinones and aromatic nitroso compounds are effective in both Hevea and Butyl rubber. *t*-Butyl perbenzoate and cumene hydroperoxide are particularly effective in Hevea rubber and GR-S containing channel black, and when used in optimum amounts, do not adversely affect tensile strength. Hexachlorocyclopentadiene and hexachlorophenol are effective in both Hevea and Butyl rubber, 1,3-Dichloro-5,5-dimethylhydantoin and hexachlorocyclopentadiene are effective in Butyl containing channel or furnace blacks. Chemical promoters are believed to initiate allylic or alkyl radicals on rubber chains, which react with active centers on carbon black, forming primary valence bonds.

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THE ABRASION OF RUBBER *

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1. INTRODUCTION

In the course of investigations into the abrasion of rubber, model experiments have recently been carried out¹, in which the conditions thought to obtain in the interface between rubber and abrasive were simulated. This was done by scratching rubber with a needle under controlled conditions, and the ensuing surface damage was found to depend markedly on the type of rubber compound employed. The general characteristics of the needle traces could be qualitatively explained in terms of the mechanical strength and the elastic and frictional properties of the samples, and various mechanisms were observed by which particles of rubber can be detached from the bulk under localized stress concentrations, such as may be expected to occur where the high particles of the abrasive impinge on the rubber surface. The needle traces gave necessarily an exaggerated picture of the extent of the surface damage produced in abrasion, but not necessarily a wrong picture of its mechanism. It will be shown here that similar results are obtained under milder conditions when the stress concentrations are brought about by friction; on the basis of this and a very few other assumptions, expressions for the dependence of abrasion on normal load and on the nature of the abrasive are deduced and compared with experimental results.

The same line of approach is shown to lead to an explanation of the origin and properties of the so-called abrasion pattern. This phenomenon has been described before²; it consists of a system of nearly parallel ridges at right angles to the direction of abrasion often found on abraded rubber surfaces. Theoretical relations connecting the spacing of the abrasion pattern with normal load and coarseness of the abrasive are now given and tested experimentally.

2. THE MODEL

When a sharp point is pressed on to a rubber surface and is set into tangential motion, a surface traction is produced on the rubber, either because the point has punctured the surface and has become mechanically entangled with the rubber, or because of frictional adhesion. In the most severe of our experiments the load per abrasive particle was only 7 grams, under which thrust even a needle will not penetrate the surface of rubber compounds of the type used. We attribute, therefore, the tangential stress initiating surface failure mainly to friction. The stress will be inhomogeneous and extremely complicated, but a qualitative picture for the two-dimensional analog can be obtained by means of a photoelastic experiment. Figure 1 (Plate I) shows a cylindrical frictional glider of 30 mm. diameter exercising the tangential force given by its limiting friction on one of the end faces of a sheet of transparent rubber 19 mm. thick.

* Reprinted from the *Proceedings of the Physical Society*, Part B, Vol. 67, pages 883-891 (1954).

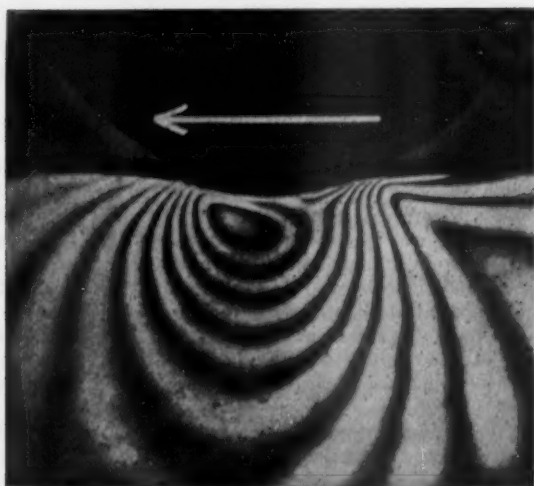


FIG. 1.—Photoelastic picture of stress distribution in rubber under tangential traction of frictional glider (sodium light).

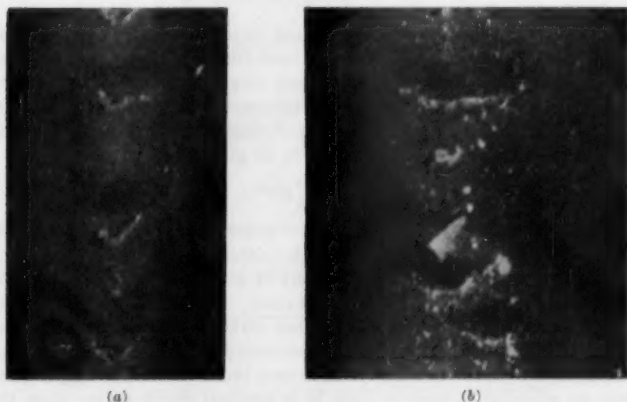


FIG. 2.—Traces of a blunt point of 1 mm. diameter under a load of 80 g. on unloaded natural-rubber vulcanisates of (a), $M_{300} = 12 \text{ kg.-cm.}^{-2}$ ($\times 18$) and (b), $M_{300} = 21 \text{ kg.-cm.}^{-2}$ ($\times 40$). M_{300} = stress per original cross-section at 300% elongation. Direction of motion downward.

PLATE I.

The sample was photographed in sodium light between crossed Polaroid sheets and quarter-wave plates, so that only isochromatics are visible. The isochromatics clearly indicate a stress concentration at the rear edge of the glider, and since the concentration occurs near the free surface, the rubber must be under tensile stress immediately behind the glider. If the rubber fails, tearing at right angles to the direction of motion would be expected. That this is so has been shown by means of an experiment carried out with the same apparatus with which the needle scratching experiments had been made, the needle having

been replaced by a hemispherically ended wire of 1 mm. diameter. The rubber compounds employed for this purpose were relatively soft in order to keep the normal loads within bounds (*cf.* Equation (1)). Two typical traces are shown in Figure 2 (Plate I), which gives photomicrographs of the surface damage on two unfilled vulcanizates of natural rubber. The traces are similar to some of the traces produced by a needle³.

Once a tear is opened, a particle will eventually be detached from the bulk during successive passes of the abrasive by any of the mechanisms discussed in detail¹. In order to arrive at theoretical expressions for the abrasion, the following assumptions are made. (1) The length of the tear opened by the abrasive particle is proportional to the width of the area of contact between the abrasive particle and the rubber. This assumption is suggested by Figure 2, where the tears appear to be confined in length to the width of the trace of the blunt point marked by a faint roughening of the rubber surface. (2) The volume of the detached rubber particle is proportional to the third power of the length of the original tear, irrespective of the way in which the particle is finally removed.

If the mean diameter of the area of contact is a , the normal load W , the mean radius of curvature at the tip of the abrasive particle where it is in contact with the rubber r , and G an elastic constant characterizing the rubber, it follows from simple dimensional considerations that

$$a/r = \text{const. } (W/Gr^2)^\alpha \quad (1)$$

where the exponent α has to be determined experimentally. The justification for introducing mean values for a and r , and for assuming that the elastic behavior of the rubber can be described by a single constant will be given presently. If there are n^2 abrasive particles per unit area, and the normal load per unit area is L so that $W = L/n^2$ then the abrasion per unit area, A , should, according to assumptions (1) and (2) above, be given by

$$A \propto n^3 a^3 = \text{const. } n^3 r^3 (L/Gn^2 r^2)^{3\alpha} \quad (2)$$

The physical properties of the rubber enter Equation (2) as G and as a factor, contained in the constant, which indicates how many passes of the abrasive are necessary for the detachment of a rubber particle, and which is, therefore, a measure of the abrasion resistance. This problem is not dealt with in the present paper. It must be pointed out that the elastic properties of loaded rubber compounds depend pronouncedly on previous deformations to which the samples have been subjected⁴ and it has been shown⁵ that the top layer near an abraded rubber surface is in general much softer than the bulk material because of the repeated large deformations occurring there. The effective value of G in Equation (2) is, therefore, different from that found with conventional measurements.

3. THE AREA OF CONTACT

In order to arrive at the value of α to be used in Equations (1) and (2), recourse was had to a model experiment in which a large sample of rubber, 25 mm. thick and 10 cm. in diameter, was indented by a hemispherical indenter of 25 mm. diameter. By ruling equidistant lines on the rubber and having a transparent indenter made of Perspex, the diameter of the area of contact could be read off directly. The results of these measurements on seven different compounds, the composition of which is given in the Appendix, are reproduced

in Figure 3, where the diameter of the area of contact is plotted against the cube root of the indenting load. It is seen that, with this method of presenting the results, straight lines are obtained which very nearly pass through the origin. The parameters of the lines were obtained by the method of least squares. The relation between a and W may, therefore, be expressed to a good degree of approximation by the equation $a \propto W^{1/3}$. It is interesting to note that this equation is the same as that given by Hertz for materials having ordinary elasticity. An easily accessible account of Hertz's work can be found

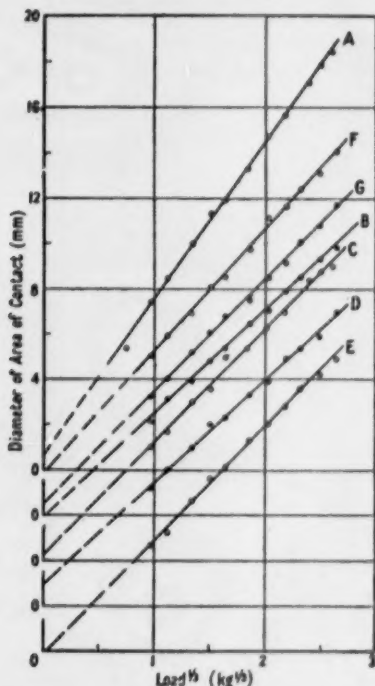


FIG. 3.—Diameter of area of contact plotted against cube root of normal load. For clarity, the curves are plotted from different origins.

in Timoshenko's book⁶, where it is also shown that, in the general case of a non-spherical indenter, the area of contact is an ellipse, the axes of which again obey the cube root law. This is taken as sufficient justification for having introduced in Equations (1) and (2) the mean radius of curvature r and only one elastic constant, G .

4. THE LOAD DEPENDENCE OF ABRASION

Introducing the exponent $\alpha = 1/3$ into Equations (1) and (2) gives

$$a = \text{const. } (Wr/G)^{1/3} \quad (3)$$

and

$$A = \text{const. } Lr/G \quad (4)$$

Equation (4) gives the simple result that the abrasion should be proportional to the normal load. The experimental test of this relation was carried out on a straight abrasive track of about 60 cm. length and with samples similar to those described before⁷. A slight modification was to mount the track on frictionless rollers, allowing longitudinal motion, but the track was held back against the frictional force exercised by the moving sample by a leaf spring, whose deflection was a measure of the friction. The abrasive employed was garnet paper⁸. All samples were extracted with acetone and vacuum-dried, for otherwise mobile impurities oozed out of the rubber and not only falsified the results but made them erratic. For the same reason, the abrasive was only used once.

In order to prevent the formation of an abrasion pattern which would increase the abrasion because of the secondary effects², the samples were reversed

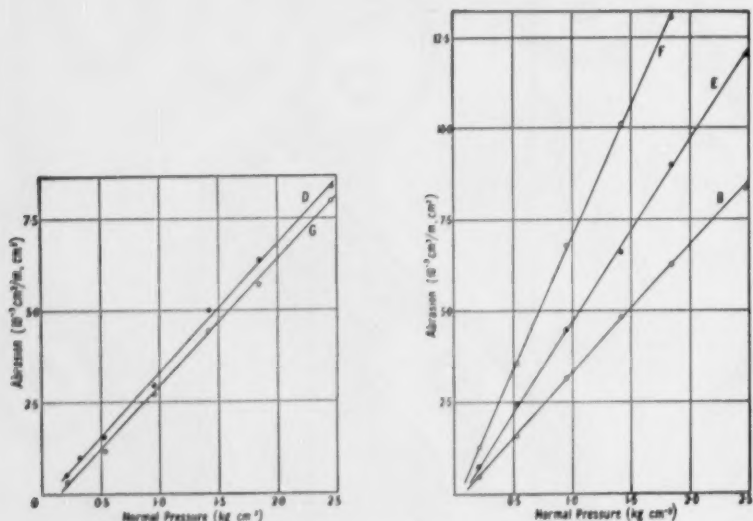


FIG. 4(a) and (b).—Abrasion plotted against normal pressure of compounds B, D, E, F and G.

after each run. The sliding velocity was $0.66 \text{ cm. sec}^{-1}$, and the rate of abrasion was determined by weighing after each two runs, making an abrasive path of 128 cm. The number of individual measurements at each load depended on the absolute value of the loss, and the reproducibility of the data lay within ± 3.5 per cent.

The results for four differently loaded compounds of natural rubber and one of Krylene (Cold GR-S) are shown in Figures 4(a) and 4(b), where they are plotted as loss in cm^3 . per 1 m. abrasive path and 1 cm^2 . surface against normal pressure. All these samples were compounded to have similar hardnesses so that any effects due to spreading out under varying loads would be small and similar; no unfilled compounds were investigated for this reason. All the experimental points in Figure 4 fall on straight lines within the limits of error, but the lines when produced do not pass through the origin. The prediction of a linear relation between abrasion and normal load as given by Equation (4)

is, therefore, largely fulfilled, apart from a small divergence at low loads. The probable explanation of this discrepancy is that, because of the irregularities of both surfaces, new contacts are made when the load is increased from very low values, thus increasing the total area of contact above that given by Equation (3). This would agree with the frictional behavior to be described in Section 6.

5. THE INFLUENCE OF THE ABRASIVE

According to Equation (4), the abrasion should be proportional to the mean effective radius of curvature of the abrasive particles so that, when comparing abrasions on different grades of the same abrasive, the relation between particle size and radius of curvature ought to be known. There appears to be no a priori reason why the sharpness of the corners of polyhedral particles should depend on their size, and it is assumed that, to a first approximation, the radius of curvature is independent of size; the abrasion would, therefore, be expected to be independent of the grade of abrasive.

An experimental test was carried out with three grades of garnet paper, the particle size having been determined under the microscope by measuring a number of randomly chosen particles after they had been dissolved off the paper.

TABLE I

Grade of abrasive Particle size (mm.) Normal pressure (kg.-cm. ⁻²)	1 1/2 40E 0.63	1/0 80E 0.29	5/0 180E 0.13
Abrasion (10 ⁻³ cm. ³ /m.-cm. ²)			
Compound D			
0.53	1.81	1.76	1.60
1.84	8.97	6.82	6.09
Compound E			
0.53	3.23	2.97	2.00
1.84	13.70	12.05	10.05
Compound G			
0.53	2.11	1.83	1.43
1.84	10.10	7.50	5.96

Three different compounds were abraded on these papers under two different normal loads each. The results, given in Table I, show that the abrasion does increase with increasing particle size in a manner which appears to depend on the compound, but the relative increase is at most only 70 per cent for an almost five-fold increase of particle size. Part, at least, of the observed departure from the predicted independence on particle size could be due to the larger particles having rather more rounded corners.

Abrasion experiments on a different type of surface will be discussed separately in Section 8.

6. FRICTION ON AN ABRASIVE

It has been shown⁷ that the frictional force of rubber is proportional to the true area of contact between rubber and track, and that, on smooth glass, the area of contact is proportional to $L^{2/3}$. It will be seen that in this case the area of contact obeys an equation identical with Equation (3). It has been stressed by Lodge and Howell⁹ that the frictional force of an elastic solid depends on the geometry of the track surface, this being in marked contrast to the friction of ordinary solids which is governed by their plastic flow properties.¹⁰ If the frictional glider is a sphere, large compared with the asperities of the elastic solid, it is easily shown on the basis of Hertz's theory¹¹ that the true area of

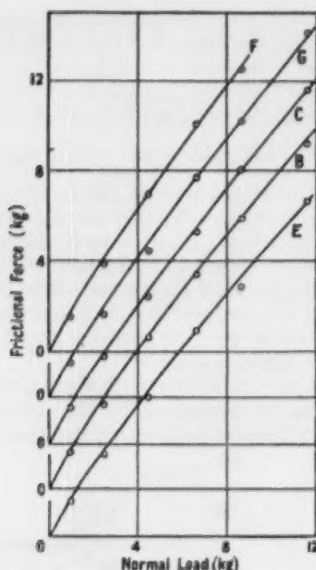


FIG. 5.—Frictional force plotted against normal load, with the following values of ϕ : B, 1.75; D, 1.765; E, 1.66; F, 1.86; G, 1.80.

contact is proportional to $W^{2/3}$, where W is the load on the glider. According to our concept of the nature of the abrasive, this result can be applied to the frictional force F between rubber and abrasive:

$$F = \phi L^{2/3} \quad (5)$$

where ϕ is a constant involving, among other things, the dimension of the asperities, elastic constant of the rubber and interfacial energy between rubber and track.

Our results are shown in Figure 5, where the full lines have been calculated according to Equation (5), with ϕ adjusted to give the best fit at high normal loads. The experimental points tend to fall somewhat below the theoretical curve at low normal loads. This is thought to be due to the same cause as the low abrasion values in this region discussed in Section 4.

For many practical purposes, the coefficient of friction on an abrasive can be considered as constant so that, to the same degree of approximation, abrasion may be said to be proportional to the work done on the rubber. It is interesting to note that Powell and Gough¹² advocate abrasion measurements at constant power input for the road wear assessment of tire compounds.

7. THE ABRASION PATTERN

The mechanism of rubber abrasion as envisaged in Section 2 begins with the opening of a number of tears in the path of the abrasive particles, which, on subsequent passes of the abrasive, are propagated in such a manner as to separate a rubber particle from the bulk. During this process, the front edge of the tear will be elongated in the direction of motion of the abrasive, similar

to the things pulled out by a needle, as shown in earlier work¹². The lip formed in this way will cover one or more tears in front, which will thus be protected from further damage; when the lip has snapped back the abrasive can attack another uncovered tear. A periodic structure will be produced on the surface, which has the characteristics of the abrasion pattern already described². In particular, the structure will develop gradually and will be the more pronounced, the softer the rubber.

If the abrasion pattern originates in this way, the dependence of the spacing of the ridges on normal load and on the grade of the abrasive can be estimated. The extent of the lip, which determines the spacing, must depend on the volume involved in the elementary abrasion process which in its turn has been assumed in Section 2 to be proportional to a^3 . For dimensional reasons, the spacing s should then be proportional to a , so that from Equation (3):

$$s \propto (Wr/G)^{1/3} \propto (Lr/n^2G)^{1/3} \quad (6)$$

According to this expression, s increases only with the cube root of the normal load; the properties of the abrasive enter Equation (6) with r and also with n , i.e., the grade of the abrasive. For the present purpose, the connection between n and the particle size d is given with sufficient accuracy by the Equation: $d = 1/n$, and the spacing should increase with $d^{2/3}$. As for the variation of r with particle size, this can be deduced from the observed increase of the abrasion with increasing particle size as given in Section 5. The experiments described below have been carried out on the garnet papers 1 1/240E and 5/0 180E; the average ratio of the abrasions on these two papers is 1.445 which, if totally attributed to the increase of r , means, according to Equation (4), that the effective radii of curvature have the same ratio. The relative increase of the spacing due to this reason would be, from Equation (6), equal to $1.445^{1/3}$, i.e., 1.10.

Abrasion patterns were produced on three different compounds at a velocity of 6.60 cm.-sec⁻¹. This velocity is higher than was used for the abrasion measurements, because the patterns develop better at higher rates of sliding. The reason for this effect is not properly understood. On the coarse abrasive, the patterns tend to be obscured by heavy scoring marks, which limit the scope of these experiments to a certain extent. The results are given in Table 2, where the values of the spacings are averages of eight counts. Examples of abrasion patterns developed under various conditions are shown in Figure 6 (Plate II).

TABLE 2

Particle size of abrasive (mm.)	0.13	0.63 spacing (cm.)	r_s
Normal pressure (kg.-cm. ⁻²)			
Compound C			
0.53	0.0123	0.0398	3.23
1.84	0.0183	—	
r_L	1.49		
Compound D			
0.53	0.0145	0.0470	3.24
1.84	0.0191	—	
r_L	1.315		
Compound E			
0.53	0.0147	0.0508	3.45
1.84	0.0211	0.0795	3.75
r_L	1.435	1.565	

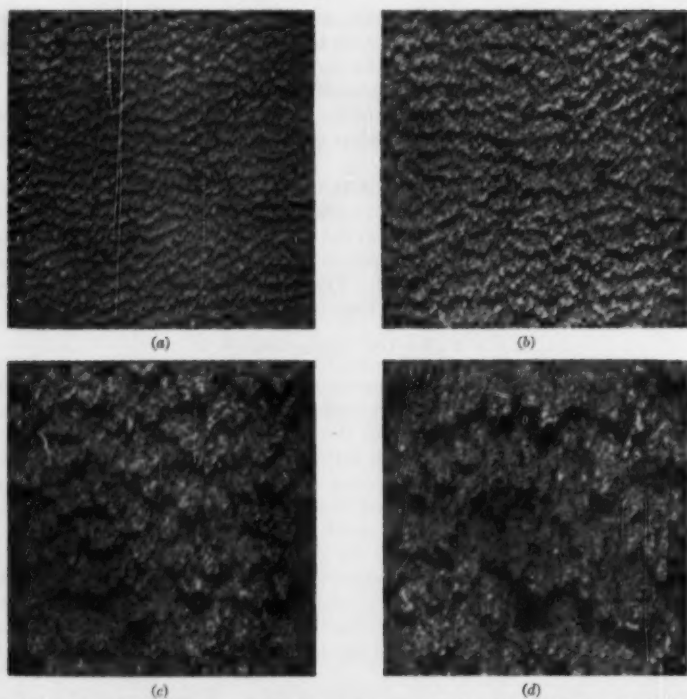


FIG. 6.—Abrasion patterns on compound E. Normal pressures: (a) and (c) $0.53 \text{ kg.-cm.}^{-2}$; (b) and (d), $1.84 \text{ kg.-cm.}^{-2}$. Abrasives: (a) and (b), 0.13 mm.; (c) and (d), 0.63 mm. ($\times 14$)

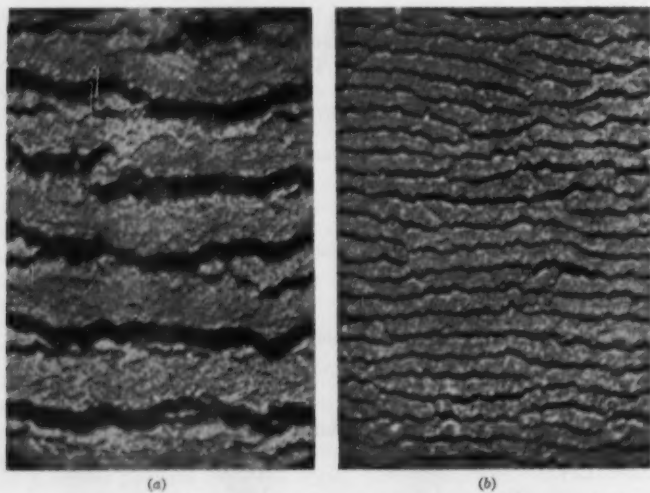


FIG. 7.—Abrasion patterns formed on concrete road surfaces. (a), coarse, and (b), fine surface. ($\times 14$)

The magnification employed when photographing the coarse patterns is actually too high for these surfaces, but it is desirable to show all patterns at the same magnification. In Table 2, r_L is the ratio of the spacings produced under the loads of 1.84 and 0.53 kg.-cm.⁻². The theoretical value of r_L is $(1.84/0.53)^{1/3} = 1.515$. r_a is the ratio of the spacings produced on the two abrasives, the theoretical value of which is $1.10(0.63/0.13)^{2/3} = 3.10$. When comparing the theoretical ratios with those given in Table 2, it will be seen that the theory is at least qualitatively borne out by experiment.

8. ABRASION ON ROAD SURFACES

If the abrasive can be approximated to a set of close-packed hemispheres, so that $r = 1/n$ in Equation (3), it follows from Equations (4) and (6) that

$$A/s = (L/G)^{2/3} \quad (7)$$

Abrasion and spacing of the pattern are, therefore, proportional to each other with this type of abrasive. However, the value of A in Equation (7) is the abrasion determined in the absence of a disturbing abrasion pattern, and in principle A and s should be determined in separate experiments.

A set of hemispheres can, perhaps, serve as a model of a concrete surface consisting of sand or gravel embedded in cement. A few abrasion measurements have been carried out on two experimental concrete road surfaces in the

TABLE 3

Surface	Coarse	Fine	Ratio
Abrasion (10 ⁻³ cm. ² /m.-cm. ²)	1.57	0.41	3.88
Spacing (cm.)	0.832	0.234	3.56

grounds of the Road Research Laboratories at Narmondsworth. These surfaces cannot be specified in quantitative terms, and they will simply be described as very coarse and very fine. Only one compound, C, was abraded on both surfaces, and it was not practicable to reverse the direction of abrasion during the experiments. As a consequence, pronounced abrasion patterns were formed on both surfaces, which are reproduced in Figure 7 (Plate II). The values of the abrasions under a normal pressure of 1.65 kg.-cm.⁻² and at a sliding velocity of 48 cm.-sec.⁻¹, and the lengths of the spacings produced at the same time are given in Table 3.

The good agreement between the ratios of abrasions and spacings shown in Table 3 is to a certain extent misleading, since the abrasion patterns will have increased the abrasions on the two concrete surfaces to different extents. But even if this effect is allowed for by reducing the abrasion ratio by, say, 20 per cent, there is still substantial agreement with Equation (7), and comparison of the results obtained on garnet papers of different grades with the results in Table 3 demonstrates the important bearing of the nature of the abrasive on the laws of abrasion.

CONCLUSIONS

The most sweeping assumption made in our theoretical approach to the abrasion problem is that all rubbers are subject to the same abrasion mechanism irrespective of polymer and filler. Nevertheless, it will have been seen that the naive conceptions put forward in Section 2 lead to predictions which are at least qualitatively borne out by the experimental findings. It would appear, therefore, that the assumptions which have been made are essentially correct and thus provide a basis for a quantitative approach.

SUMMARY

Theoretical results on the abrasion of rubber have been deduced from a few simple assumptions concerning the initiation of the surface damage. The abrasion is proportional to the normal load, independent of the particle size of the abrasive if the particles are polyhedral, and proportional to their mean radius of curvature if they can be approximated to hemispheres. The spacing of the abrasion pattern is proportional to the cube root of the normal load, proportional to the two-thirds power of the particle size on an abrasive with polyhedral particles, and directly proportional to the particle size on an abrasive with hemispherical particles.

These predictions have been reasonably well confirmed by experiment.

ACKNOWLEDGMENTS

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APPENDIX

Composition of Samples

	A	B	C	D	E	F	G
Smoked sheet	100	100	100	100	100	100	—
Krylene	—	—	—	—	—	—	100
Zinc oxide	5	5	5	5	5	5	5
Sulfur	2.5	3	2.5	2.5	2.5	2.5	1.8
Stearic acid	1	3	2.5	3	3	1	3
Dutrex-R	—	—	—	2	2	—	2
Pine tar	—	—	4.5	—	—	—	—
Santocure	0.6	—	0.5	0.7	0.7	0.7	1.1
M.B.T.	—	1	—	—	—	—	—
P.B.N.	1	1	1	—	—	—	—
Nonox-HFN	—	—	—	1	1	1	1
Filler	—	50 MPC	50 HAF	50 HAF	75 FT	130 W	50 HAF
Cure	—	—	—	—	—	—	—
(min. at 140° C)	50	50	40	35	40	20	80 at 150° C

Notes and abbreviations: Krylene is a low-temperature polymerized copolymer of butadiene and styrene; Dutrex-R is a mineral oil; M.B.T. (mercaptobenzothiazole) and Santocure are accelerators; P.B.N. (phenyl-2-naphthylamine) and Nonox-HFN are antioxidants; HAF = high abrasion furnace black; MPC = medium processing channel black; FT = fine thermal black; W = Pattinson's activated CaCO₃ (whiting).

MOONEY VISCOSITY CHANGES IN FRESHLY PREPARED RAW NATURAL RUBBER *

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In the course of investigations carried out in connection with the technical classification of natural rubber, large permanent increases of Mooney viscosity of the order of 30 to 40 units have been observed when freshly prepared raw or masticated rubber is stored under conditions of low relative humidity.

The rate of change and the extent of the increase are both affected by the relative humidity of storage, and the effects are most pronounced in the region below about 30 per cent relative humidity. The rate of change in dry air increases with decreasing thickness of the sample and with rise of temperature, although these effects are masked somewhat by oxidative breakdown on prolonged storage at temperatures higher than about 30° C. Mooney values continue to increase long after the rubber has reached constant weight on drying; the removal of acetone-soluble and nitrogenous nonrubber components and of oxygen does not prevent the changes from taking place. The effects are only partially reversed by subsequent storage at high relative humidity, and there is evidence to suggest that the hardening is associated with the development of a cross-linked benzene-insoluble gel structure throughout the rubber.

The rate of mill breakdown of dry stored rubber is greater than that of fresh rubber, but in comparisons by means of a fixed breakdown procedure, the hardened rubber has a higher Mooney value after mastication. Rubbers hardened by storage in dry air exhibit slightly improved properties after vulcanization in the form of a pure-gum mixture, even after the additional breakdown required to reach normal levels of viscosity.

Fluctuation of temperature and humidity in commercial smoke houses and drying sheds may well account for a part of the variability of natural rubber when measured by Mooney viscosity determinations of the freshly prepared product, and different conditions of storage will add a further contribution to the total hardness variation encountered by the consumer.

* Reprinted from the *Archief voor de Rubbercultuur*, Extra No. 2, pages 149-150, October 1953. This paper was presented at the Conference of Rubber Research Institutes in the Far East, held at Bogor, Java, July 15-17, 1952. The complete paper was not published in the special issue of the *Archief*, and this version is a summary of the paper of R. I. Wood.

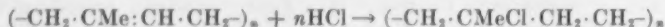
EVIDENCE FOR A HYDROCHLORINATION RETARDER WITHIN NATURAL-RUBBER LATEX PARTICLES *

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One of several features revealed by extensive kinetic studies of the hydrochlorination of rubber latexes¹ is strong evidence for the presence of a retarder, very probably a basic substance, inside the particles of Hevea latex. Apart from the biological interest of this finding, it has important technical implications. Almost all rubber used industrially is first transformed chemically, usually by vulcanization. The rates of sulfur vulcanization of different specimens of Hevea rubber are notoriously variable. The sulfur chloride vulcanization of crepe rubber solution in the absence of accelerators was shown by Glazer² to have an initial slow period in kinetic experiments. These facts suggest that retarders, possibly varying in amounts from specimen to specimen, may affect vulcanization reactions of Hevea rubber.

Experimental details on the preparation of synthetic polyisoprene latex have been published previously³. A typical formulation is as follows: isoprene, 4 grams; water, 5 grams; 20% Vulcastab LW (non-ionic stabilizer) in water, 1.5 gram, ammonium persulfate, 0.085 gram. These ingredients are shaken for 270 minutes at 57° C, and then freed from residual isoprene monomer. The hydrochlorination reaction is schematically represented:



It is carried out in a microreactor by keeping the thermostatically controlled sample of latex saturated with HCl under a fixed pressure of HCl gas, as described in detail earlier⁴.

The graph representing the progress of hydrochlorination of a synthetic polyisoprene latex with time starts with an almost vertical jump representing a fast reaction⁵ confined to the surface of the dispersed particles. This initial jump is followed by the main linear portion of slope k_2 , indicating a zero-order reaction which continues until nearly all the hydrocarbon is fully converted (Figure 1, plot I). Hevea latex (Figure 1, plots III and IV) shows a similar behavior, though the initial jump in the graph is lower because of the smaller specific surface of rubber hydrocarbon available for reaction. The jump is joined to the main linear portion of slope k_2 by a slower linear portion of the rate plot, with slope k_1 ($\sim 0.3k_2$), representing a period of retarded hydrochlorination. The zero-order rate plots and the identity of the slopes k_2 for the different natural and synthetic substrates show that the rate-controlling step is a purely inorganic one; it has been interpreted³ as the rate of formation of a reactive ion pair (H^+ , Cl^-) in the rubber particle from suitable precursors. Every time such an ion pair is formed, it is instantaneously snapped up by reacting with a double bond of the rubber. Details of the rapid reaction step involving the polymer are not relevant to the present purpose.

* Reprinted from the *Journal of Applied Chemistry*, Vol. 5, Part 2, pages 62-64, February 1955.

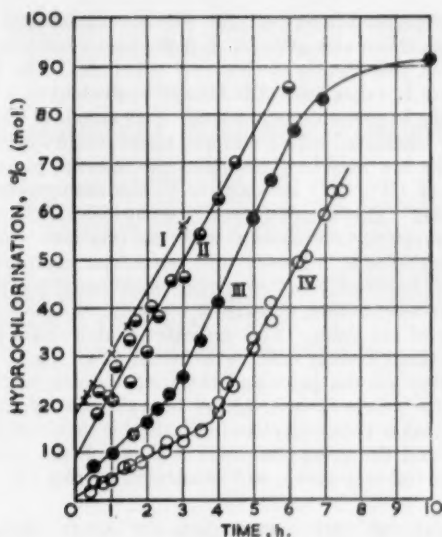


Fig. 1.—Hydrochlorination-rate curves of polyisoprene latexes. I. Synthetic polyisoprene latex at 69.5° and 1.95 atm. HCl. II. Fine fraction of acid-creamed Hevea latex at 69.5° and 1.95 atm. HCl. III. Normal Hevea latex at 69.5° and 1.95 atm. HCl. IV. Normal Hevea latex at 0° and 1 atm. HCl.

CONSTANCY OF THE TOTAL RETARDATION EFFECT

Figure 2 presents rate plots for Hevea latex hydrochlorination under six different conditions of temperature and HCl pressure. Only the main line of slope k_2 is drawn in each case, and extrapolated back to zero time as a broken line. Numerous experimental points relating to the early parts of the reactions, i.e., the linear portions of slope k_1 , have been omitted for simplicity. It is

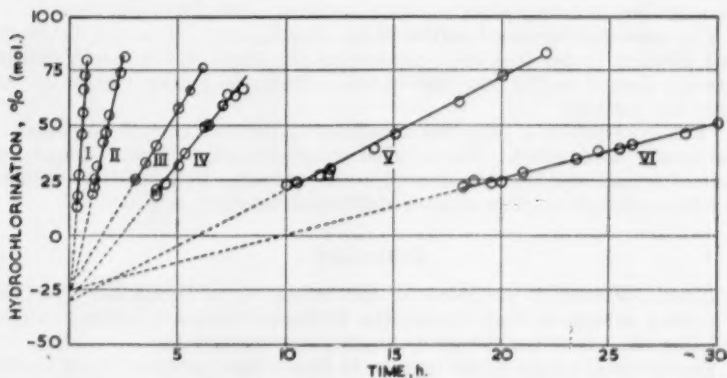


Fig. 2.—Extrapolation of main rate (k_2) to composition axis. I. Hevea latex at 0° and 2 atm. HCl. II. Hevea latex at 26.7° and 2 atm. HCl. III. Hevea latex at 69.5° and 1.95 atm. HCl. IV. Hevea latex at 0° and 1 atm. HCl. V. Hevea latex at 26.7° and 1 atm. HCl. VI. Hevea latex at 69.5° and 0.91 atm. HCl.

seen that the extrapolated lines converge within experimental error to a single point on the composition axis at -27 ± 3 per cent (mol.) hydrochlorination. The explanation of this kinetic observation is simple. The total retardation before the full rate k_2 takes control is always equivalent to a fixed proportion (27 per cent) of the isoprene units present. This supports the hypothesis that the retardation is associated with a material agent inside the particles. For on this hypothesis the law may be stated that the retarder present deactivates a constant weight of (H^+ , Cl^-) irrespective of the temperature, pressure, and rate of the reaction. This constant weight is, however, far too large to reflect merely a stoichiometric combination with the retarder. From the analysis of Hevea latex particles it is known that nonrubber components are present only in traces. (The effect is not concerned with serum components.) Thus, each molecule of retarder must deactivate a considerable but (on the average) constant number of ion pairs. This indicates that a chain reaction of some kind is involved, though many different schemes arise; e.g., the chain reaction could involve either the ion pairs and the rubber units, or the ion pairs and the retarder. Two points of interest are brought out by Figure 1: the fact that retardation rather than complete inhibition⁶ is involved (i.e., $k_1 > 0$ over a range of 70°), and the great sharpness with which the retarded-rate curve goes over into the full-rate curve, well illustrated by plot IV.

REMOVAL OF THE RETARDER BY ACID CREAMING OF FINE PARTICLES

Earlier attempts at reducing the retardation effect by preliminary creaming of the latex under ammoniacal conditions were completely unsuccessful⁴. On the assumption that the retarder was likely to be a basic substance inside the particles, it was expected that extraction of the finest available particles with acid would furnish the most favorable conditions for such a reduction. These conditions apply during differential creaming experiments from a serum containing about 10 per cent of HCl over extended periods. Details of such experiments are being published elsewhere⁷. Plot II of Figure 1 shows that a fine fraction of acid-creamed latex was entirely free from the retardation effect, a straight-line plot very close to that of synthetic latex being obtained.

The somewhat increased scatter of the experimental points was due to the great dilution (1 per cent solid content) of the latex; the increased positive intercept (jump) on the composition axis reflects the greater specific surface of the fine particles.

The existence of a retarding substance in the unextracted particles can thus hardly be doubted. The detailed characterization of its structure and mode of action would be a matter of much interest. It is hoped to examine later the hydrochlorination of latex of different botanical origin.

SUMMARY

Kinetic evidence is presented for the occurrence in Hevea latex particles of a trace substance that retards the hydrochlorination reaction. No retardation effect is observed with synthetic polyisoprene latex.

The chemical nature of the retarder in Hevea latex particles is not known, but it is likely to be a basic substance. Its retardation action reflects its power to deactivate the reactive precursor of the hydrochlorination reaction, which is interpreted as a form of ion pair (H^+ , Cl^-). A constant amount of

the precursor is deactivated by the retarder, irrespective of the temperature or the pressure of the hydrochlorination reaction.

ACKNOWLEDGMENT

The authors thank Professor P. D. Ritchie for his kind interest in this work.

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STRUCTURE AND RHEOLOGICAL PROPERTIES OF HEVEA LATEX GELS *

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The production of rubber articles from Hevea latex often involves a step in which the latex is set to a gel while still containing most of the water present in the latex. The gelling is effected by chemical means¹. Handling of the wet gels, which are easily deformable and possess low strength, is often necessary in technological processes, and this should not cause any permanent deformation. Some factors which control the rheological properties of these gels have been investigated in the present study.

EXPERIMENTAL

For establishing the relationship between force, deformation, and time of deformation, creep measurements have been selected. As no changes in the composition of the gel should result from the applied deformation, an outwardly directed flow of water caused by normal forces acting on the surface of the gel must be prevented. A suitable type of deformation proved to be a simple torsion of a hollow cylindrical tube of the material. When only small deformations are used, it may be assumed that a torsional couple applied to the upper plane surface produces a simple torsion proportional to the couple if the lower plane surface remains in a fixed position. In this case the shear modulus and the viscosity can be obtained from the experimental data, provided that the wall of the cylinder is thin compared with its radius. An outer radius of 2.9 cm. was used, with a wall thickness of 0.7 cm. in a cylinder 4.2 cm. high.

The cylindrical tube is obtained by gelling the suitably compounded latex in an aluminum mold. After the required gelling time, the gel is removed from the mold and the plane end surfaces are cemented to aluminum disks by means of an aqueous solution of sodium silicate or a rubber solution. Measurements are carried out with the gel immersed in a water bath at 20° C, to prevent superficial drying.

The freshly formed gel expels water spontaneously, while contracting at the same time, even when immersed in water. This instability of the fresh gel makes a rigid mathematical analysis of the creep curves intractable. After aging the gel for 24 hours, however, syneresis has come to an end and the creep curves obtained with the aged gel can be interpreted in terms of viscoelastic behavior. Still, from a practical point of view, it is of interest to investigate the rheological behavior of the gel immediately after it has been formed. To characterize the behavior as completely as possible, two types of experiments have been performed:

* Reprinted from the *Proceedings of the Second International Congress on Rheology*, Vol. 2, pages 291-295 (1954). The Congress was held in Oxford, England, July 26-31, 1953.

- (1) a short-duration test on fresh gels in which the creep curve was measured for 30 minutes and the subsequent recovery for 60 minutes;
- (2) a long-duration creep and recovery measurement extending over a period of several days, with gels that had been allowed to age for 24 hours.

RESULTS

The creep and recovery curves obtained in the present experiments are similar in appearance to the curves usually observed with visco-elastic materials. The deformation in the first second after application of the load is strikingly large, and always much larger than the corresponding instantaneous recovery from removal of the load. The considerable discrepancy between the two values must be attributed to the non-homogeneity of the material. The shear modulus has, therefore, always been calculated from the recovery curve.

With fresh gels, the deformation remaining after 60 minutes' recovery is expressed as an apparent viscosity. The viscosity of aged gels has been calcu-

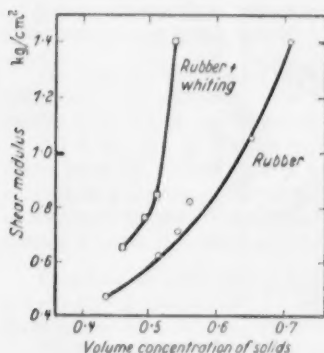


Fig. 1.—Shear modulus as a function of volume concentration of solids in fresh gels. Effect of addition of a filler. \circ rubber. \square rubber + whiting; volume ratio whiting/rubber = 0.2.

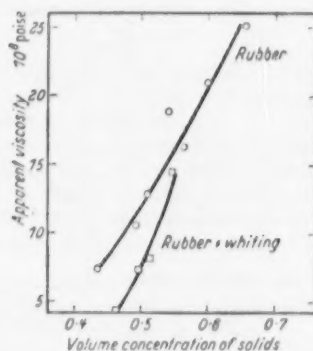


Fig. 2.—Apparent viscosity as a function of volume concentration of solids in fresh gels. Effect of addition of a filler. \circ rubber. \square rubber + whiting; volume ratio whiting/rubber = 0.2.

lated from the slope of the creep curve after the rate of deformation had become constant.

In the small range of stresses used in our experiments (10^4 to 3×10^4 dyne/cm²), no deviation from linear behavior could be detected.

Figures 1 and 2 show the dependence of the shear modulus, and the apparent viscosity on the volume concentration of rubber, in fresh gels formed by heating Hevea latex for 10 minutes at 70° C in the presence of a zinc-ammonium complex. The modulus and the apparent viscosity both decrease on decreasing the solids content of the gel from 70 to 40 per cent. The same kind of behavior is observed when part of the rubber is replaced by an indifferent filler, like calcium carbonate (whiting). The increase of the modulus and the decrease of the apparent viscosity caused by the presence of whiting have been found to be proportional to the volume ratio of whiting/rubber (Figure 3).

The apparent viscosity, and to a lesser extent the modulus, depend on the composition of the interfacial layer surrounding the particles in the gel. Re-

removal of the proteins, which occur in Hevea latex in an amount of up to 2 per cent of the weight of the rubber, results in a decrease of the apparent viscosity to half of its original value. The proteins had been removed by displacement from the interface by ammonium oleate.

TABLE I
RHEOLOGICAL PROPERTIES OF FRESH GELS
Latex gelled with zinc-ammonium complex at 70° C.
Volume fraction of rubber 0.48

Substance	Modulus (kg./cm. ²)	Apparent viscosity (poise $\times 10^{-4}$)
Original latex	0.56	10.1
Proteins displaced by ammonium oleate	0.35	5.1
As before, but with 2 per cent of egg albumin	0.44	6.3

By adding egg albumin to this "purified" latex, higher values of the modulus and the apparent viscosity are again obtained.

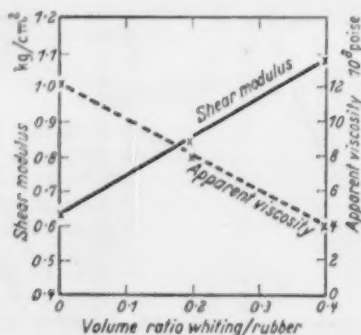


FIG. 3.—Shear modulus and apparent viscosity as functions of volume ratio whitening/rubber in fresh gels. Volume concentration of total solids = 0.51.

After aging a latex gel for 24 hours in water, the syneresis has come to an end, the final volume concentration of rubber being then between 65 and 80 per cent. A constant rate of deformation is obtained 3000 to 4000 minutes after the application of a torsion couple to such an aged gel. If, however, the rubber molecules have been cross-linked by vulcanization of the gel, this time is reduced to 1000 to 1500 minutes. (The vulcanization was accomplished by adding the necessary ingredients to the latex and heating the gel for 30 minutes in boiling water.) The retarded elastic behavior may, therefore, at least partially, be attributed to the viscoelastic properties of the rubber itself. The flow of aged gels also depends on the properties of the rubber molecules: the viscosity of a vulcanized gel appeared to be 25×10^{11} poise, while that of an unvulcanized gel is only 4×10^{11} poise, both at a volume fraction of rubber of 0.71. The shear modulus increases from 1.4 to 3 kg. per sq. cm. as a result of vulcanization of the gel. The value of the modulus is also affected by the particle-size distribution of the rubber globules. A latex having a narrow size distribution (diameter 0.1 to 0.35 micron) was obtained by fractionated creaming³. The modulus of a gel made from this latex had a value of 0.35 kg. per

sq. cm. at a volume fraction of 0.65; this is considerably lower than the value for a normal latex gel of the same rubber concentration (Figure 1).

CONCLUSION

Hevea latex is an emulsion of spherical rubber globules in an aqueous serum. The rubber particles range in diameter from 0.05 to 2.0 micron. The attractive forces between the particles are counteracted by electrostatic repulsion exerted by the ionized components of the interfacial layer. By decreasing this repulsion in one way or another, many of the particles will stick together upon collision and a three-dimensional network will be formed enclosing the serum, provided that the volume concentration of particles is sufficiently high. The gel produced in this way is not yet stable; the free energy of the system can be further reduced by increasing the number of points of contact between the particles. This causes spontaneous rearrangement of the particles in the gel, which entails expulsion of the serum.

A further decrease of the free energy might be attained by coalescence of the rubber globules, resulting in a reduction of the interfacial area.

It may be assumed, however, that coalescence of the particles will not occur in ordinary latex gels because:

(1) Coalescence will be inhibited by the presence of an interfacial layer between adjacent globules. For coalescence to occur, this layer will have to be locally removed at the places of contact between the spheres:

(2) After the interfacial layer has been locally removed and coalescence takes place by viscous flow of the rubber molecules, its rate will be small according to a theory proposed by Frenkel³. Owing to the high viscosity of the rubber and the small interfacial tension, the time of total coalescence of two rubber spheres in a latex gel will be of the order of 10^6 seconds.

Experimental evidence in favor of this assumption was obtained by electron microscopy of the surface of dried latex films, using a two-step replica technique. Even after vulcanization, the individual particles were clearly visible.

These considerations show that the wet gel possesses an inhomogeneous structure, in which the individual rubber particles have not lost their identity. The actual amount of coalescence occurring during the drying and vulcanization processes, as usual in manufacturing rubber articles from latex, has not hitherto been established, but will be rather low.

The observed behavior of latex gels can be explained on the basis of this assumption. The irreversible part of the deformation, characterized by the value of the apparent viscosity, results mainly from the displacement of the globules with respect to each other. The resistance against this flow will be a function of the number of points of contact between the particles and the binding energy of these contacts. The number is controlled by the volume concentration of the rubber and the binding energy by the composition of the interfacial layer. The influence of the proteins in this layer may be understood by assigning a cementing action to these compounds. The binding energy will, however, also be increased by occasional interlinking of rubber molecules in adjacent globules.

The reversible part of the deformation has its main source in the deformability of the rubber globules, and in the extensibility of the network formed by these particles. It follows that the modulus is a function of the intrinsic properties of the components and of the volume fraction of the various components

in the gel. It is of interest to observe that fillers behave in respect to modulus of wet gels like reinforcing fillers in vulcanized rubber.

The binding energy between a filler particle and a rubber globule in a latex gel is generally less than the energy of a bond between two rubber globules. Substitution of contacts between filler particles and rubber globules for contacts between rubber globules only will, therefore, result in a decreased resistance against flow.

After prolonged syneresis, the average inter-particle distance in the gel has become very small.

The resistance against mutual displacement of the particles has increased enormously because the number of points of contact and the binding energy between adjacent globules have both increased. The flow exhibited by the aged gels must, therefore, be attributed largely to irreversible deformation of the rubber globules. The values of the viscosity agree with the expected values in this case: 10^{11} to 12^{12} poises.

SUMMARY

Some rheological properties of hydrogels made from Hevea latex have been determined by shear measurements, using a hollow cylindrical test piece. The shear modulus and the viscosity depend on the volume concentration of solids in the gel, the composition of the interfacial layer surrounding the rubber globules, and the particle-size distribution of the rubber globules. An interpretation of the experimental results is given, based on the assumption that no coalescence of the rubber particles occurs. The rheological properties of the gel should then be functions of the number of points of contact between the particles and of the strength of the bonds between the particles in the gel.

ACKNOWLEDGMENT

This work was undertaken under the management of H. C. J. de Decker, Director of the Research Department, Rubber Foundation, Delft.

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SOLUBILITY OF ZINC OXIDE IN PRESERVED HEVEA LATEX *

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INTRODUCTION

The use of Hevea latex in the manufacture of rubber articles generally involves the addition of zinc oxide at some stage of the process. The addition of zinc oxide to the latex affects the properties of the system, e.g., an increase of viscosity or even gelation of the latex may be observed. This kind of behavior with zinc oxide is often undesirable, and methods have been described to eliminate the effect¹. On the other hand, use has been made of this property by providing a means for gelling latex. Thus, with some latexes, the addition of zinc oxide alone is sufficient to produce the desired gelling behavior. With other latexes, ammonium salts also have to be added or the nonrubber components have to be broken down by means of trypsin².

In any case it is of importance to measure and control the sensitivity of the latex with respect to addition of zinc oxide, and numerous methods have been described to satisfy this demand³. However, none of the methods proposed have been generally accepted.

In the present investigation, the reactions of zinc oxide in Hevea latex have been studied as a function of the composition of the latex serum. A relation is given between the composition of the latex, as given by its pH and its ammonia content, and the solubility of zinc oxide in the serum.

ACTION OF ZINC OXIDE IN LATEX

The action of zinc oxide in Hevea latex has been shown to depend on three consecutive reactions⁴:

(1) Dissolution of the zinc oxide in the ammoniated serum. Schematically, this may be represented as:



(2) The tetrammine complex, which is predominantly formed at normal temperature and at ammonia concentrations usually present in latex, dissociates into complexes containing less ammonia on increasing the temperature or decreasing the pH value⁵:



(3) The lower coordinated complexes form insoluble soaps with the fatty acid anions adsorbed at the surface of the rubber globules:



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in which R represents a fatty acid, and x appears to have a value⁶ of about 2.

The negative charge at the surface of the rubber globules, which is connected with the presence of adsorbed fatty acid anions, is decreased by reaction (3). This results in an increased viscosity (thickening) or even gelling, depending on the amount of zinc complex ions and fatty acid anions available.

In assigning a value to the sensitivity of latex to zinc oxide, it will have to be taken into account that the overall sensitivity is determined by the rates of three consecutive reactions. If it is assumed that the dissociation of the complex (reaction (2)) is not very sensitive to the composition of the latex, it follows that the sensitivity of latex to zinc oxide is, as a first approximation, determined by:

- (1) The amount of zinc oxide dissolving in the serum;
- (2) the amount of fatty acid anions adsorbed at the surface of the rubber globules.

In a latex showing pronounced thickening in the presence of zinc oxide, both the solubility of the zinc oxide in the serum and the amount of fatty acid present will be sufficiently large. If, however, a latex is not sensitive to zinc oxide, this may result from a deficiency either of fatty acid or zinc ammonium ions, or from both causes together. Samples of latex showing a high stability with respect to addition of zinc oxide because of either of these factors can, actually, be prepared easily. This explains the fact that one single test cannot be used to measure the zinc oxide sensitivity of latex, and tests have already been proposed which enable the rates of both reactions (1) and (3) to be estimated⁷.

The theory outlined above represents only a simplified picture of the action of zinc oxide in latex. A number of additional factors operates in affecting the actual behavior of latex containing zinc oxide. In particular, the presence of amino acids and phosphates in the serum must be mentioned, the first of which may enter the complex cation, which affects its stability and thus the amount of lower complex ions available in the serum. Phosphate ions interfere with reaction (3). The essential point, however, concerns the formation of an insoluble (undissociated) salt of the fatty acid anions with a bivalent cation produced by dissociation of the zinc tetrammine complex ion, which itself is unable to form insoluble soap at the concentrations present in latex.

The influence of these additional factors on the behavior of latex mixes may be considered as being of secondary importance, whereas the stability is mainly controlled by the reactions (1) and (3). It is an object of the present investigation to determine the solubility of zinc oxide in the serum of ammoniated Hevea latex, as a function of the composition of the serum. This allows an estimation of the contribution of reaction (1) to the zinc oxide sensitivity of latex. When the contribution of reaction (3) has also been determined, it will be possible to investigate the second order effects as described above.

COMPOSITION OF LATEX SERUM

The dissolution of zinc oxide in the serum of ammoniated Hevea latex is generally attributed to the formation of complexes with the ammonia. The serum, however, contains several other components which may enter into complexes with zinc ions, and such as amino acids⁸, and even simple anions like acetate⁹ and chloride⁹. The concentration of ammonia in latex serum is, generally, much higher than the concentration of all amino acids together; it may, therefore, be expected that the solubility of zinc oxide in the latex serum

is mainly controlled by its ammonia content. A solution of an ammonium salt containing some free ammonia will be used as a model system for investigating the solubility of zinc oxide in latex serum. The results of numerous experiments show that the behavior of zinc oxide in the model solutions is essentially the same as in the serum of Hevea latex (compare Figures 2 and 3).

The composition of a solution containing an ammonium salt together with free ammonia can be described completely by means of any two independent parameters. Suitable pairs of parameters are the pH and the "total ammonia" ($\text{NH}_3 + \text{NH}_4^+$) content, or the concentrations of (NH_3) and (NH_4^+). At the fairly high values of the pH usually encountered in latex serum, the nature of the anion contained in the ammonium salt has hardly any influence on the composition of the solution at a given pH, unless the anion is derived from an extremely weak acid¹⁰.

In latex technology, the ammonia content and the pH are generally used to describe the composition of the serum. The ammonia content, or "total alkalinity", corresponds closely with the concentration of ($\text{NH}_3 + \text{NH}_4^+$) as used in the present investigation¹⁰. The pH can be varied at constant ($\text{NH}_3 + \text{NH}_4^+$) content by varying the ratio between ammonia and ammonium salt. This is what happens in latex on the addition of acid, alkali or sodium fluosilicate. The ($\text{NH}_3 + \text{NH}_4^+$) content can also be varied at constant pH by the addition of a concentrated solution containing ammonia and ammonium salt in exactly the ratio necessary to obtain the desired pH. In this way the influence of pH and of ($\text{NH}_3 + \text{NH}_4^+$) content can be studied independently.

EXPERIMENTAL METHOD

The amount of zinc oxide which dissolves in latex serum can be determined directly by means of polarography, according to a method indicated by Casagane.¹¹ The model solution, or the compounded latex, is contained in a small beaker in which a pool of mercury serves as an anode. The usual *i vs. V* polarograms were measured, with mercury dropping at the cathode at a rate of about 0.5 drop per second.

An aqueous dispersion of zinc oxide was produced by ball-milling zinc oxide with an equal weight of a 4 per cent aqueous solution of Darvan. Weighed amounts of this dispersion were added to aqueous ammonia containing an ammonium salt. A nonionic emulsifying agent (Emulphor-O of the Badische Anilin & Soda-Fabrik) was added in an amount corresponding with 1 per cent of the weight of the final solution; this is sufficient to suppress the polarographic maximum. The pH of the final solution was measured and its polarographic behavior determined. Deaeration of the fairly concentrated solutions appeared unnecessary.

The solubility of zinc oxide in latex serum can be determined in exactly the same way, without previously separating the serum from the rubber. The latex should contain 1 per cent of Emulphor-O (calculated on the serum) to prevent thickening.

In model solutions containing a predetermined amount of dissolved zinc complex, the height of the polarographic wave was found to be directly proportional to the concentration of zinc complex if the pH and the ($\text{NH}_3 + \text{NH}_4^+$) content remained constant. Variation in the composition of the solution caused an appreciable change of the wave height caused by a given concentration of complex. In latex the situation is still more complicated, as the wave height depends, not only on the amount of dissolved complex, the pH, and the am-

monia content, but is also strongly affected by the dry rubber content and by other factors which have not been studied in detail. Though it would appear possible to determine the amount of zinc complex dissolved from the wave height obtained in a latex containing an excess of solid zinc oxide, this procedure would involve the introduction of a number of corrections. A more direct method has, therefore, been adopted, in which the solubility of zinc oxide is obtained from the position of the break in the curve obtained by plotting the wave height *vs.* the amount of added zinc oxide (Figure 1).

The zinc oxide used was a commercial sample of fairly high purity, as had been found by comparing its solubility in aqueous ammonia with that of various other samples. The zinc oxide used in these experiments had the lowest solubility of all the samples available. Ammonia was of analytical grade, and was used shortly after dilution of the concentrated stock solution. Other reagents were of analytical grade.

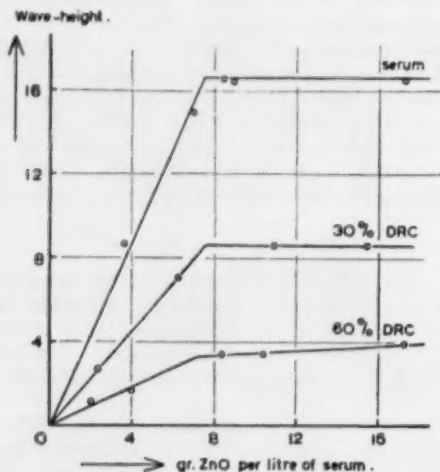


Fig. 1.—Determination of the absolute value of the solubility of zinc oxides in latex.

The ammonium salt used in this investigation was the chloride. Addition of glycine, or substitution of glutamic acid for part of the chloride, had no perceptible influence on the height of the polarographic wave.

Experiments were conducted at room temperature, which was about 20° C. Reproducibility of the results was generally better than 10 per cent, which was considered sufficient for the present purpose. The half-wave potential was at about -1.5 volt, but depended somewhat on the composition of the liquid. This phenomenon has not been further investigated.

RESULTS

When measuring the solubility of zinc oxide directly in latex, the height of the polarographic wave is affected by the rubber content of the latex. This is shown by the data assembled in Figure 1, which have been obtained in an old ammoniated field latex and in the cream and serum produced therefrom by creaming by means of alginate. The ammonia content of both cream and

serum were found to be 0.547 M, and the KOH numbers 0.290 M for the cream and 0.228 M for the serum; all concentrations expressed as equivalents in the aqueous phase. The higher KOH number of the cream is due to fatty acids adsorbed at the surface of the rubber globules.

Because of this slight difference in KOH number, the parameters determining the solubility of zinc oxide will not have quite the same value for the various samples, but this effect is much smaller than the experimental error. The absolute value of the solubility of zinc oxide in the serum of the various samples was determined by polarographic analyses of the samples compounded with increasing amounts of zinc oxide. It was found that the addition of more than 7.5 grams of zinc oxide per liter of serum did not result in a further increase of the wave height, showing that the solubility of zinc oxide in the serum was about 0.092 M, independent of the amount of rubber present.

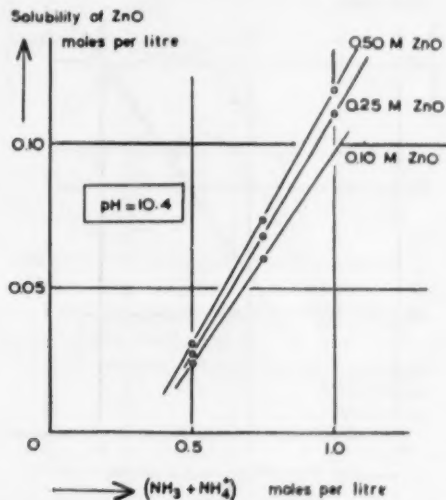


Fig. 2.—Solubility of zinc oxide in model solutions depends on the amount of zinc oxide added.

The zinc oxide, as it is obtained commercially, contains varying amounts of anions, generally sulfate, especially carbonate¹². The dissolution of the zinc salt in the aqueous ammonia occurs according to the equation:



Comparison with the equation representing the dissolution of zinc oxide (Section 2) shows that less hydroxyl ions will be formed when the zinc oxide used is contaminated with anions. This results in a lower pH of the final equilibrium mixture. As will be shown below, this will increase the solubility of the zinc oxide under the conditions prevailing in ammoniated latex. It follows that this solubility will depend on the amount of zinc oxide present as a solid phase, as is shown in Figure 2, which relates to experiments performed with model solutions.

Addition of an "indifferent" electrolyte, like potassium sulfate, has a negligible effect on the solubility of zinc oxide in latex serum.

In contradistinction to the considerable effect of the time of contact between zinc oxide and latex serum, which has been reported in the literature¹¹, no increased solubility could be found after having allowed the dispersed zinc oxide to dissolve for times longer than 10 to 15 minutes. It is believed that no such time effect exists if contact with the atmosphere is rigorously excluded.

The effect of the $(\text{NH}_3 + \text{NH}_4^+)$ content on the solubility of zinc oxide, at constant pH, appears from Figure 3. These results were obtained with a latex which had been purified by creaming repeatedly, and in which the $(\text{NH}_3 + \text{NH}_4^+)$ content was varied by addition of a mixture of ammonia and ammonium chloride. It is important to note that substitution of phosphate, acetate, or carbonate for the chloride as the anion of the ammonium salt did not affect the results.

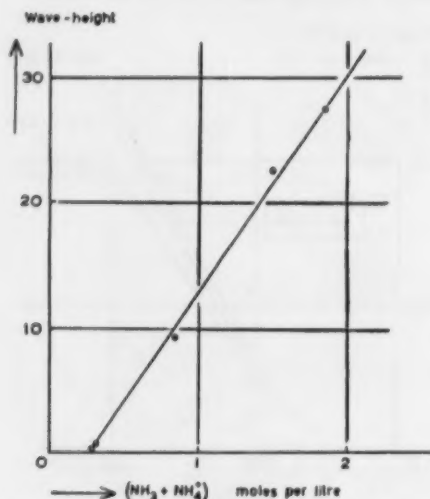


Fig. 3.—Relation between the solubility of zinc oxide in latex and the concentration of $(\text{NH}_3 + \text{NH}_4^+)$, at constant pH.

Figure 4 shows the effect of pH, at constant $(\text{NH}_3 + \text{NH}_4^+)$ content, on the solubility of zinc oxide in model solutions containing ammonia and ammonium chloride. Similar results have been obtained in latex. The significance of the maximum in the solubility occurring at a pH of about 9.4 will be discussed in the following section.

DISCUSSION

The overall reaction between zinc oxide and ammonia, as formulated in Section 2, would suggest that the solubility is proportional to the fourth power of the (NH_3) concentration and inversely proportional to the square of the (OH^-) concentration. Jordan¹² concluded from this equation that the solubility of zinc oxide can be decreased by decreasing the (NH_3) concentration or by increasing the pH. The influence of these important variables can now be studied more quantitatively.

It should be realized that the concentrations used in equation (a) of Section 2 are those in the final equilibrium mixture, whereas, in Figures 2 to 4, concentrations have been used as they occur in the serum before the addition of zinc oxide. From a practical point of view, it is of importance to express the solubility of zinc oxide in a given latex as a function of the composition, determined by normal routine methods. The results of the present investigation suggest that the zinc oxide solubility is solely determined by the concentrations of (NH_3) and (NH_4^+) as they occur in the original latex, before the addition of zinc oxide. The relation describing the zinc oxide solubility as a function of the initial concentrations of (NH_3) and (NH_4^+) can be found, in principle, from a consideration of the equilibria involved. The resulting expressions are

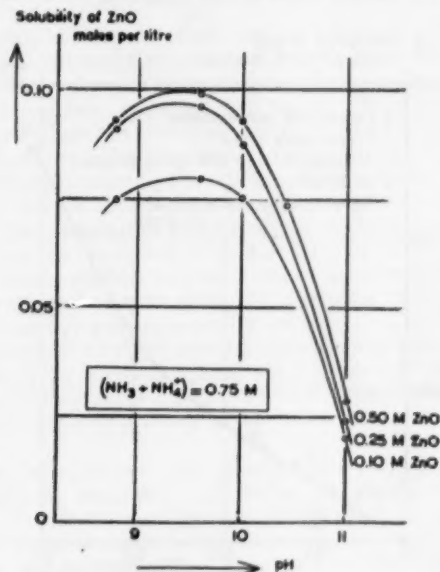


FIG. 4.—Effect of pH on the solubility of zinc oxide in model solution containing ammonia and ammonium chloride.

highly complicated, and not suitable for further analysis. Moreover, they do not take into account the effect of the anions generally present in commercial zinc oxide. A useful approximation may, however, be found from the experimental results recorded in Figures 2 to 4.

At a constant pH, and thus a constant concentration of (OH^-) ions, the solubility of zinc oxide is proportional to the original free ammonia content of the latex. This proportionality has been shown to exist between the solubility and the concentration of $(\text{NH}_3 + \text{NH}_4^+)$, but at a constant pH the ratio between (NH_3) and (NH_4^+) is also constant, and it follows that the concentration of (NH_3) is proportional to that of $(\text{NH}_3 + \text{NH}_4^+)$.

The effect of an increased (OH^-) concentration at constant concentration of $(\text{NH}_3 + \text{NH}_4^+)$ is used experimentally in the application of the KOH number test, in which the pH is increased by the addition of fixed alkali, thus keeping the

ammonia concentration constant. To study this effect more quantitatively, it must be taken into account that decreasing the pH, even at constant "total ammonia" content, will also decrease the (NH_3) concentration. This will counteract the solubilizing effect of the decreased pH. The solubility will, in this case, be controlled by some function of the concentrations of (NH_3) and (OH') , which may show extreme values.

From the maximum of the solubility at a pH of about 9.4 shown in Figure 4, it may be concluded that, on decreasing the pH from 11 down to 9.4, the solubility is increased because the change in the (OH') concentration has more effect than the corresponding decrease of the (NH_3) concentration. At lower values of the pH, however, the variation of the (NH_3) concentration appears to be more important. From a consideration of the equilibria involved, it becomes ap-

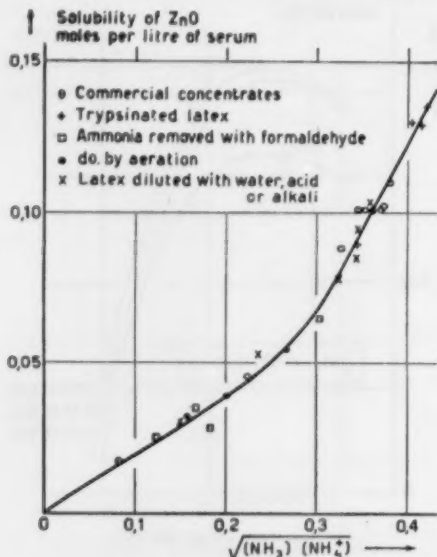


Fig. 5.—Relation between composition of latex serum and zinc oxide solubility.

parent that the function given by the (NH_3) concentration divided by the square root of the (OH') concentration shows a maximum value at pH 9.3. It would follow that the solubility of zinc oxide may be described by a linear function of $(\text{NH}_3) (\text{OH}')^{-1/2}$ or, by selecting another pair of parameters:

$$S = f' \cdot \sqrt{(\text{NH}_3) \cdot (\text{NH}_4^+)}$$

The concentration of ammonium ions in latex serum can be determined most conveniently by subtracting the concentration of (HCO_3') ions from the KOH number¹⁰. Evidently, the latter should be expressed in suitable units, i.e., in equivalents per liter of aqueous phase. In a number of latex samples of widely differing composition, the concentrations of (NH_3) and (NH_4^+) have been determined analytically, and the results have been correlated with the polarographically determined solubility of zinc oxide in Figure 5.

The relation between the zinc oxide solubility and the geometric mean of the concentrations of free ammonia and of ammonium ions is not linear over the whole range of concentrations investigated, though the deviation from linearity is not considerable if the mean concentration is not varied to a large extent. From these results it may be concluded that the zinc oxide solubility is, as a first approximation, determined by the product of the initial concentrations of (NH_3) and (NH_4^+). If the presence of another component affecting the zinc oxide solubility were assumed it would follow that the effect of this component is constant in a large number of commercial latex samples of varying origin, and not affected by treatments of the latex as applied in the present investigation. It is, evidently, more convenient to assume that the non-rubber components, apart from (6H_3) and NH_4^+ , do not affect the zinc oxide solubility to an appreciable extent.

The solubility of zinc oxide in all commercial samples of ammonia-preserved concentrate was between 0.09 and 0.12 moles per liter of serum. Deviating values have only been found in very old or in badly spoiled samples, and also in samples which had been preserved with agents different from ammonia. The considerable variability in overall sensitivity towards zinc oxide, which may be found in different samples of ammonia-preserved concentrate, appears to be connected with differences in the activity of the complex (reaction (3) of Section 2) rather than in the amount of complex available for reaction.

Several of the commercial latex samples have been treated in various ways, and the effect of the treatment on the zinc oxide solubility has been recorded in Figure 5. Treatment with trypsin increases the concentration of ammonium ions from the original value of about 150 millimoles per liter of serum to values between 220 and 250 millimoles per liter of serum. The free ammonia content has been reduced, at constant concentration of ammonium ions, by addition of formaldehyde or by aeration. At a "total alkalinity" of 0.5 per cent, corresponding to a free ammonia content of about 150 millimoles per liter of serum, the zinc oxide solubility is about 25 per cent of the solubility in the untreated latex.

Of practical importance is the effect of a decreasing pH at constant ($\text{NH}_3 + \text{NH}_4^+$) content, such as occurs during the gelling of latex with sodium fluosilicate. It follows from Figure 4 that the solubility of zinc oxide increases until the pH value of about 9.4 has been obtained, and decreases again if the pH decreases still further. The maximum solubility obtained at a pH of 9.4 depends very much on the total ammonia content, and can be decreased considerably if the ammonia content has been reduced by air-blowing or by addition of formaldehyde.

Actually, by reducing the "total alkalinity" to 0.35 per cent (of the serum), the solubility of zinc oxide at a pH of 9.4 may be decreased to one-fifth of the value which would occur in the fully ammoniated latex.

SUMMARY

The solubility of zinc oxide in Hevea latex, and in model solutions containing an ammonium salt together with free ammonia, has been measured by means of polarography. It is found that the solubility, at a given value of the pH, is proportional to the concentration of ammonia and ammonium salt together. At a constant concentration of ammonium ions plus free ammonia, the solubility shows a maximum at pH 9.4. A relation between the solubility of zinc oxide in Hevea latex and the concentrations of ammonium ions and free

ammonia is given. The relation is checked with a number of latex samples of varying origin, and with samples produced therefrom by the addition of silicofluoride, formaldehyde, or trypsin.

ACKNOWLEDGMENT

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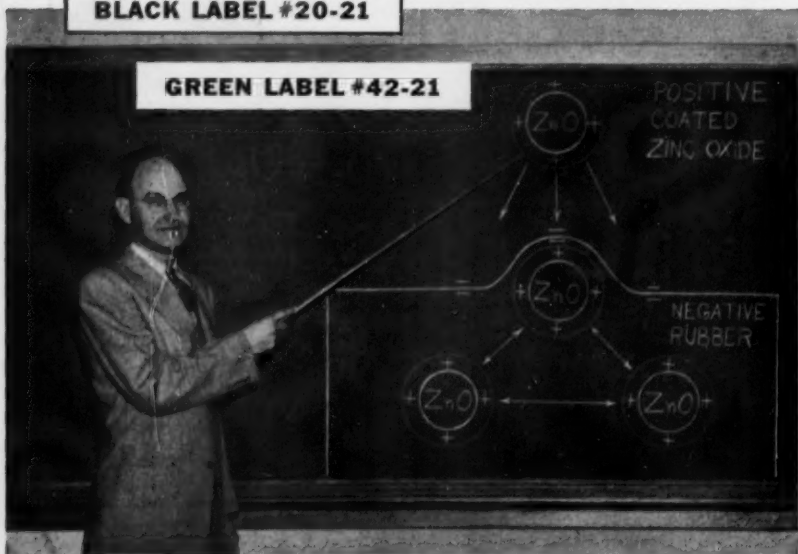
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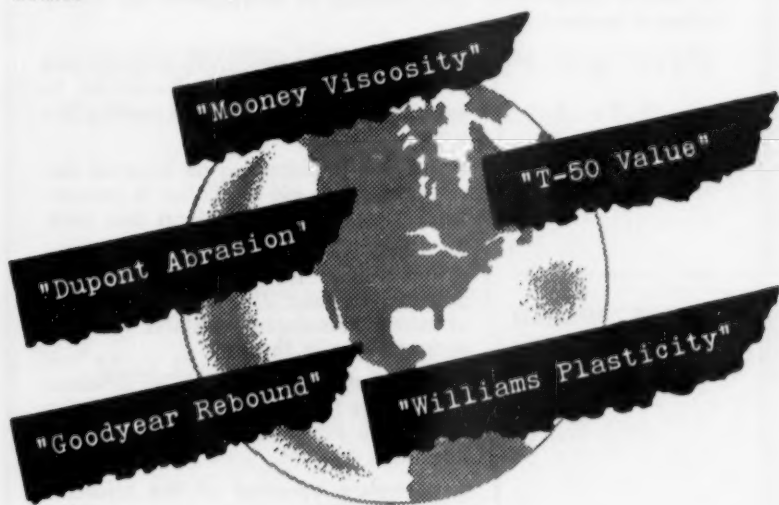
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INDEX TO ADVERTISERS

	PAGE
Aleo Oil and Chemical Corporation	25
American Cyanamid Company, Organic Chemicals Division	12
American Zinc Sales Company	23
Cabot, Godfrey L., Inc.	13
Carter Bell Manufacturing Company, The	29
Columbia—Southern Chemical Company	25
Columbian Carbon Company (opposite Table of Contents)	20
Du Pont, Elastomers Division (Chemicals)	11
Du Pont, Elastomers Division (Neoprene)	34
Goodrich, B. F., Chemical Company	22
Goodyear, Chemical Division	5
Goodyear, Chemical Division	9
Hall, C. P. Company, The	10
Harwick Standard Chemical Company... (Inside Back Cover)	
Huber, J. M., Corporation	31
Koppers Company, Inc. (Chemical Division)	15
Monsanto Chemical Company	7
Naugatuck Chemical Division (U.S. Rubber Company)	17
Neville Chemical Company	14
New Jersey Zinc Company, The... (Outside Back Cover)	
Pan American Refining Corporation, Pan American Chemicals Division	8
Pennsylvania Industrial Chemical Corporation	16
Phillips Chemical Company	2
Rare Metal Products Company	29
Richardson, Sid, Carbon Company	6
Rubber Age, The	33
Rubber World	28
St. Joseph Lead Company	26
Scott Testers, Inc.	27
Sharples Chemicals, Inc.	3
Southern Clays, Inc.	30
Stamford Rubber Supply Company	24
Sun Oil Company, Sun Petroleum Products	
(Opposite Title Page)	18
Superior Zinc Corporation	29
Thiokol Corporation, The	4
Titanium Pigment Corporation	31
United Carbon Company... (Inside Front Cover)	
Vanderbilt, R. T. Company	21
Witco Chemical Company... (Opposite Inside Front Cover)	1

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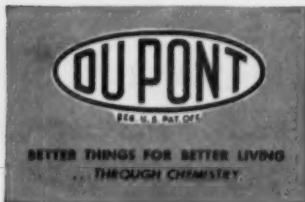
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